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HISTORY OF RESEARCH AND DEVELOPMENT OF THE CHEMICAL WARFARE SERVICE IN WORLD WAR II (1 July 1940 - 31 December 1945)

Project 4-72-05-005

Volume 4

STERNUTATORS

by

Benjamin Witten
Edward M. Wharton

25 October 1954

Copy No. 54

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Army Chemical Center
Maryland

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Volume 4

STERNUTATORS

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PREFACE

Selection and presentation of data for the history of research and and development in the Chemical Warfare Service in World War II were guided by the requirements set forth in the memorandum dated 1 August 1944, ASF SPROD, subject: History of Wartime Research and Development. In accordance with this directive, the historical monographs have been written with the objective of furnishing:

A guide to future research and development personnel to prevent or discourage repetition of unsuccessful investigations.

A ready reference text or source book for research and development personnel to indicate a line of research and development to be followed or avoided.

A source of information for personnel charged with the preparation of military characteristics.

A source of information to those responsible for the initiation or approval of development projects to be used as a background for approving or disapproving project initiation.

A factual text for historians and others requiring correct information on the many varieties of research and development projects undertaken during the war.

A reference manual for staff planners to assist them in the preparation of future war plans.

In general, these monographs provide a complete history of Chemical Warfare Service wartime research and development, focused particularly on the work done from 1 July 1940 to 31 December 1945. In many cases it was not possible to conclude the story of the latter date, and wherever possible the completed story was continued to the date of last revision.

Volume 4 of the series endeavors to give a complete factual account of the development of sternutators, as carried out by the Chemical Warfare Service and other war agencies.

These monographs were begun under the direction of Major Clarke Robinson, CWS, Chief Historical Branch OC, CWS and continued under the supervision of Dr. Leo Finkelstein, Editor-in-Chief, Historical Branch, OC, CWS. In June 1947 their completion was turned over to the Chemical Corps Chemical and Radiological Laboratories.

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CONTENTS

ILLUSTRATIONS

C.C.T.C.	Chemical Corps Technical Committee
C.P.	Chemical Production Section, American University Experiment Station, Research Division
CRLTL	Chemical and Radiological Laboratories Technical Library
D.S.	Dispersoid Section, American University Experiment Station, Research Division
ETF	Edgewood Technical Files
G.M.R.	Gas Mask Research Section, American University Experiment Station, Research Division
NDRC	National Defense Research Committee
O.R.	Offense Chemical Research Section, American University Experiment Station, Research Division
P.R.	Porton Report
S.O.R.	Sutton Oaks Report

INTRODUCTION

Irritant Smokes. Irritant smokes have variously been called toxic smokes, vomiting gases, sternutators, and irritant smokes. This report will be concerned only with those solid or liquid substances which can be dispersed as a particulate cloud and whose symptomatology is similar to DM and DA. This report will not cover other toxic smokes, such as cadmium oxide and cadmium chloride, or other agents which incidentally cause nausea or vomiting such as chloropicrin.

The following effects of exposure to DA are noted in order of appearance: irritation of nose and throat, irritation of the eyes with lacrimation, irritation of the chest with a growing feeling of suffocation, an occasional nasal secretion, and nausea. If exposure is prolonged, aching pains in the stomach and numbness of the limbs may appear. This numbness may later give rise to extremely sharp pains. Subsequent to exposure the following systems are often exhibited: dizziness, profuse salivation, intense burning in the nose and throat, nausea, headache, and toothache. The burning pains in the nose and throat persist after all other effects have disappeared (1).

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1. "A Digest of Reports Concerning the Toxic Effect of Diphenylchloroarsine," Edgewood Arsenal Chemical Division (hereinafter EACD) 127, p. 2, 5 Apr 1922.

CHAPTER I

Historical Background

Use of Sternutators in World War I

The everlasting struggle between armor-piercing shell and the protecting armor of a battleship was paralleled during World War I in chemical warfare. The weak places in a defense must first be discovered. In order to destroy an armored battleship, either its defenseless bottom is attacked by torpedoes, or its protecting armor penetrated by armor-piercing explosive shell.

In chemical warfare it was a struggle between the gas mask and poisonous gases. The weakness in the gas mask in 1917 was due to the fact the chemicals in the canister sorbed only true gases. The molecules of true gases are in a very active state of motion and soon strike against any walls with which they come in contact. If the walls are granulated, as in the case of the charcoal used in the gas mask canister, the available area of walls against which the molecules strike is increased and holds the molecules of the heavier gases in its pores. However, if the air contains poisonous substances, not as molecules, but in the form of clusters of molecules (for example, dust or smoke), the clusters are not very active in the current of air (except for Brownian movements), but hover like pieces of driftwood in a river. Consequently, they seldom touch the walls of the charcoal and therefore do not adhere to them. For this reason, smoke passed almost unhindered through the filter of the gas mask used by the Allies in 1917.

The Germans, in their search for a substance in the form of smoke, came to the aromatic series of the arsenic compounds, among which there were chlorodiphenylarsine and cyanodiphenylarsine (2).

$(C_6H_5)_2AsCl$	$(C_6H_5)_2AsCN$
chlorodiphenylarsine	cyanodiphenylarsine

These compounds were solids with negligible vapor pressure. They were dispersed by heavy explosive charges, in the form of a finely pulverized dust. The particulate clouds thus created lasted only a few minutes in the open, and they were accordingly classed as nonpersistent agents. They were, however, immediately effective and readily penetrated the existing gas masks of the Allies. It was due chiefly to these properties that they were introduced by the Germans on the night of July 11, 1917 (3).

2. "The Use of Arsenical Compounds During the World War," Office Chief, Chemical Warfare Service, p. 1, 8 May 1933. (In files of Chemical and Radiological Laboratories, Technical Library, Army Chemical Center, Md. (hereinafter CRLTL), as ETF 011-7).

3. Augustin M. Prentiss, Chemicals in Warfare (New York: McGraw-Hill Book Company, Inc., 1937), p. 202.

Chlorodiphenylarsine was first used by the German Army at Niewport on 11 July, 1917, in the form of a 12% solution in phosgene and diphosgene (Green Cross #2). In September 1917 a combined high explosive and chlorodiphenylarsine shell containing 18% to 22% DA and the remainder high explosive was introduced (Blue Cross shell). In June 1918 cyanodiphenylarsine replaced chlorodiphenylarsine because of its alleged greater stability towards water and its supposed greater effectiveness.

The number of shell containing chlorodiphenylarsine (Blue Cross) used by the Germans was estimated at from several hundred thousand to fourteen million. The amount of chlorodiphenylarsine manufactured was 3,000 tons. During the last few months of the war, 600 tons of chlorodiphenylarsine was manufactured monthly.

The use of chlorodiphenylarsine by the Germans was a deliberate attempt to penetrate the canister of the gas mask, because the increased protection afforded the steadily improved masks and the better gas discipline offset the German use of lung irritants in the Green Cross shell. To the Germans it meant such an advance of offensive tactics over protection that the effect on the Allies would be almost as if they were entirely unprotected. The masks then in use by the Allies afforded practically no protection against particulate clouds, and the failure of the German hope can be due only to the very poor dispersion with resulting low concentration and large particle size of the chlorodiphenylarsine from the Blue Cross shell (4).

The German tactics were to use the toxic smokes for offensive purposes. The Blue Cross shell was first fired on those areas to be attacked by the Germans in order to make the defenders remove their masks as a result of the irritation and violent sneezing caused by inhalation of the toxic smokes. The bombardment was immediately followed by Green Cross shell (phosgene and diphosgene) in order to cause severe casualties when the defenders were unprotected (5).

The Germans continually increased the use of the Blue Cross shell and claimed great results for it. The following instructions issued from the German GHQ over Ludendorff's signature on 9 July, 1918 expresses the German viewpoint on the Blue Cross shell:

> The substance in Blue Cross shell acts with extraordinary rapidity, in fact almost instanteously, but it generally puts troops out of action for only a short time. In sufficient concentration it penetrates the French mask effectively and the English mask to a lesser degree, in which case it forces the enemy to tear off their gas masks.... In the case of an insufficient concentration,

4. "Irritant Smokes, Preliminary Investigation," Edgewood Arsenal Technical Report (hereinafter EATR) 286, pp. 1-3, 18 Nov. 1938.

5. ETF C11-7, pp. 2-3.

> Blue Cross at least forces the enemy to wear their masks, thereby interfering with their fighting efficiency. The effect of the gas passes away and rapidly disappears after the gas or detonation cloud. In consequence it can be employed when our infantry are relatively close to it.

No fatal cases of poisoning by chlorodiphenylarsine or cyanodiphenylarsine occurred in the British Army in France, but the casualties reported were significant. Thus in the British Fifth Corps Gas Center (which may be taken to represent the southern half of the British front), between 25 May and 30 June, 1918, the percentage of Blue Cross casualties was 17.3%, while in the same hospital from 25 May to 19 October, 1918, out of a total of 3,510 gas cases admitted, 9.6% were Blue Cross and 7.0% were Green Cross (lung irritant) casualties. In the No. 7 Stationary Hospital (which derived most of its casualties from the northern half of the British front), Blue Cross causalites accounted for 9.5% and Green Cross for 5.7%. The figures derived from these two sources are in close agreement. During the last two or three months of the war the increased proportion of Blue Cross shell used by the Germans led to an increase, though not a marked one, in the number of Blue Cross casualties. The American figures are not so complete. Out of 70,000 gas cases in the AEF, "arsine" accounted for 577 with 3 fatalities.

The chemical advisor to the 5th Corps (British) summarized the effects of the Blue Cross shell in the following words:

> It is a negligible menace so far as causing serious and prolonged casualties; but it is a very real factor in a battle, particularly in a retreat, where both its moral and physical effects may greatly influence the issue during a limited number of hours.

He further expressed the opinion that anything beyond a mild dose led to a general decrease in the stamina and power of resistance, and thus contributed to the number of prisoners taken by the enemy (6).

Towards the end of the war the Allies placed a mechanical filter consisting of wadding and layers of felt in their canisters and in this way provided adequate protection (7).

From the above study it is apparent that the principal uses of chlorodiphenylarsine or similar arsenicals in shell for artillery were for neutralization of machine gun fire, counterbattery and long-range bombardment, disruption of lines of communication, and interference and slowing down of working parties. Against an enemy who had inadequate protection, the arsenical smoke was claimed to break down his resistance (8).

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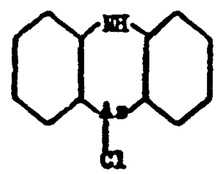
6. EATR 286, pp. 1-2, 4.

7. ETF 011-7, p. 4.

8. EATR 286, p. 4.

The Allies studied the possibilities of retaliating against the Germans. The German process for the manufacture of chlorodiphenylarsine was so complicated, however, that it was soon realized that a simpler method of making it must be developed. In seeking to find such a method, the British and American chemists simultaneously discovered in 1918 that a slightly different, though closely related, compound could be easily manufactured in large quantities, and that this substitute compound had very similar properties and seemed to be equally effective as a respiratory-irritant chemical agent. This new compound was diphenylaminechloroarsine.



Diphenylaminechloroarsine (DM)

The Americans named this compound "Adamsite," after its American discoverer, Major Roger Adams (9).

Neither diphenylaminechloroarsine nor the other arsenicals were manufactured in time by the Allies for use during World War I.

Development of Sternutators in World War I

Dispersion of Smokes by Explosives. A research program was carried out at the American University during World War I to determine the factors contributing to smoke formation on explosion of a shell. Three designs of shell were investigated. These were:

1. The mixture type, in which the toxic agent was intimately mixed with the explosive.

2. The long burster type, in which the toxic agent surrounded a long burster containing explosive.

3. The German type (Blue Cross), in which the explosive in the shell surround a container holding the toxic agent.

The Mixture Type.

Ratio of Explosive to Smoke-Producing Material. In work at American University during World War I the optimum weight ratio of explosive

9. Prentiss, op. cit., p. 211, 212.

to smoke-producing material was seen to depend upon the following factors:

a. Relative distribution of the two substances.

b. Strength of container.

c. Nature of smoke material and explosive.

When intimate mixtures of DA and TNT were used it was found that only a small variation in the percentages of explosive and smoke-producing material was possible, if good detonation was to be retained on one hand and good smoke concentration on the other. If more than 30% of the mixture was DA, the detonation of the TNT became difficult; if less than 15% DA was used, the cloud differed little in density and toxicity from TNT smoke along. When the percentage of DA was close to 30%, excellent smoke clouds of large size and good density were obtained.

For intimate mixtures of finely powdered DM and TNT in 75-mm. shell the mixtures having 55% to 60% DM were found to be the best both for smoke production and good detonation and fragmentation.

A study of the stability of mixtures of DA and TNT showed that mixtures of this type were of questionable stability and not entirely safe for use in a shell. Test to determine the stability of DM and TNT carried out at 65°C. showed that for a period of 2 wk. no development of pressure was evident.

A comparison of results for bombs of weak containers (paper), and strong containers (iron pipe), showed that for weak containers the higher the ratio of explosive to agent (up to 3:1), the greater the dispersion efficiency, while the ratio for strong bombs showed the reverse to be the case. The differences, however, were not large, especially for the strong bombs.

For a given type of bomb, a given amount of explosive was capable of scattering only a limited amount of material in a state fine enough to remain in suspension. Any attempt to use less than the critical amount of explosive resulted in a lessened efficiency (10).

Strength of Shell Wall. The strength of the shell wall is one of the most important factors in determining the size of the smoke particles. The quantity of smoke produced from a given bomb is greater when the material is enclosed in a strong container than when in a fragile one.

In bombs using DA and TNT made from either paper bags or iron pipes, about twice as much smoke was obtained from the iron containers as from the

10. EATR 286, p. 5, 6; "The Use of Mixtures of DM and TNT in 75-Mm. Shell for the Production of Toxic Smokes," American University Experiment Station Research Division (Washington, D. C.) Dispersoid Section (hereinafter D.S.) 150, 17 Dec 1918; "The Dispersion of CA by the Explosive Method," D.S. 90, 21 Aug 1918; "The Mixture Type of Dispersoid Shell," D.S. 114, (Undated); "Density and Rate of Settling of DA," D.S. 9, 18 May 1918.

paper bags (11).

Density of Loading. The density of loading in a projectile is defined as the weight of the charge divided by the inclosing space. In experiments in which 10 g. of TNT and 10 g. of DA were loaded into bombs of sizes varying from 2.4 cu.in. to 18.1 cu.in. and the density of loading consequently varied from 0.0675 to 0.52 g./ml., it was found that the density of the smoke produced was directly proportional to the density of loading.

Effect of Powdering and Compressing Smoke-Producing Material. In a comparison of powdered DM with cast DM in a 75-mm. shell, it was found that either melting the DM or using extremely high pressure in packing, i.e. high density gave poorer results than hand tamping the powdered DM.

Effect of Temperature and Addition of Heat-Producing Agents. Heating the smoke-producing material before explosion was found beneficial in increasing the density of smoke. Thus, raising the temperature of DM from 20° to 150°C. resulted in a rise of 82% in the smoke density. For DA raising the temperature from 20° to 100°C. resulted in a 13% increase.

The addition of powdered aluminum in an explosive to increase the heat content of the mixture so as to give better smokes was investigated. Explosives of this character are known as ammonals, and usually contain from 3% to 20% aluminum powder. In the above experiments the ammonals varied from 2.5% to 30% aluminum powder, 20% TNT, and 55% to 77.5% ammonium nitrate. It was found that the addition of aluminum had little, if any value (12).

The Long-Burster Type.

The burster type of shell as developed at the American University consisted of a long central core of explosive surrounded by the smoke-producing material. Static tests were made of the long-burster shell employing different diameter burster tubes. The penetrating power of the smoke from the different types of shell was found to rank as follows (those of greater penetrability first):

11. EATR 286, p. 7; D.S. 90; "A Comparison of the Quantity of Smoke Obtained From Similar Bombs Enclosed in Fragile and Strong Containers," D.S. 89, 20 Aug 1918; "The Dispersion of DA by the explosive Method Using TNT and Tetryl," D.S. 80, 8 Aug 1918; "Penetration of G-76 Smokes Made by Explosive Dispersion in a 10 cu.m. Box," D.S. 115, 21 Oct 1918.

12. EATR 286, p. 9; "Comparison of the Smokes Produced by Three Samples of DM," D.S. 46, 28 Jun 1918; "The Production of DM Smoke From 75-mm. Shell," D.S. 159, 23 Dec 1918; "Effect of Temperature on the Efficiency of Production of Smokes by Explosive Dispersion," D.S. 51, 10 Jul 1918; "Effect of Aluminum Upon the Dispersive Power of an Explosive," D.S. 95, 11 Sep 1918.

1-7/16-in.-diameter burster (1.2 DA to 1 TNT)

1-in.-diameter burster (5.3 DA to 1 TNT)

1-1/2-in.-diameter burster (1.2 DA to 1 TNT)

1-3/4-in.-diameter burster (0.56 DA to 1 TNT)

The complete characteristics of the best long-burster-type shell, as shown by the above test, were as follows: (13)

Type shell	Mk 1
Weight of explosive (TNT)	260 g.
Weight of DA	315 g.
Void	10%
Diameter of burster	1-7/16 in. o.d.
Length of burster to weld	7.87 in.
Material of burster	Shelby seamless steel tubing
Thickness	16 gauge (0.0625 in.)
Bottoming of burster	Direct contact
Thread in shell nose	U.S. standard
Gas seal	Lead washer and paint

German Type.

Blue Cross. The German type of Blue Cross shell consisted of a bottle, or container, of DA inclosed in explosive. The description of the various types is as follows:

77-mm. Blue Cross

Weight of DA	135 g.
Weight of explosive (TNT)	620 g.
Volume of bottle	100 ml. (approx.)
Ratio of DA to TNT	0.22:1

13. EATR 286, p. 11, 12; "Development of a Shell for Efficient Dispersion of DA and Similar Toxic Substances," D.S. 155, 25 Jan 1919; "Protection Afforded by Various Canisters Against DA Shells," American University Experiment Station Research Division (Washington D.C.) Gas Mask Research Section (G R) 684, 7 Oct 1918.

105-mm. Blue Cross

Weight of DA - - - - - - - - - - 370 g.

Weight of explosive (TNT) --- 1280 g.

Volume of bottle - - - - - - - 300 ml. (approx.)

Radio of DA to TNT - - - - - - 0.29:1

In the 155-mm. shell a cylinder containing DA was set into a hollow space in the explosive charge, with magnesia cement. In the 21-cm. shell the DA was placed in a tin can. The ratio of DA to explosive was 0.5:1.

A comparison of the dispersing efficiency of a Blue Cross shell was made in static firing with various other types. It was found to be inferior to either the long-burster type or the mixture type.

Green Cross 2. The Germans also used a shell filled with 12% to 15% solution of DA in phosgene and diphosgene. This shell was made in 15- and 21-cm. sizes. The object of this shell was to use both an irritant and lethal agent in the same shell. This shell was largely replaced by the Blue Cross. The disadvantage in the use of a solvent for DA or DM is that it cuts down the amount of the agent in the shell and therefore diminishes the concentration of the particulate cloud (14).

The "M" Device. The most efficient method of dispersing DA, DC, and DM was by condensation of a supersaturated vapor. When volatilized by heat, the vapor condenses to form extremely small particles, having a diameter of the order of magnitude of 10^{-4} to 10^{-5} cm. On the other hand, when dispersed by explosion, the dispersion of the chemical was due almost entirely to the physical force of the explosion. The explosives normally used, such as TNT, did not have a sufficiently large energy content to vaporize the smoke-producing material, in spite of the fact that they liberate all their energy in a very short space of time. Thus, 1 kg. of petroleum has a heat of combustion of about 12,000 cal., coal about 8,000 cal., and dry wood 3,500 to 4,000 cal., while TNT in exploding has only 710 cal. The result was that particles dispersed by explosion were usually many times larger than those resulting from heat distillation. Similarly, when the compound was dissolved in a liquid solvent and sprayed by a mechanical sprayer, even the best sprayers sent out droplets many times larger than the true smoke particles.

These facts were apparently not appreciated by the Germans at the time they adopted chlorodiphenylarsine as a filler for their irritant smoke shell, for they first attempted to dissolve this compound in some easily volatilized solvent, such as diphosgene, and disperse it as a liquid spray. When this proved unsatisfactory, they attempted to disperse it by the use of heavy charges

14. EATR 286, p. 14.

of high explosive, which also subsequently proved inefficient on the field of battle. In loading chlorodiphenylarsine into the shell, another error was made in placing the explosive charge around, instead of within, the chemical charge. With the explosive surrounding the chemical charge, the force of explosion tended to compress the chemical particles, instead of blowing them apart.

The British were active during the latter part of World War I in pushing the development of a toxic candle which would by progressive burning distill off the chemical as a true smoke, in which form it was found to be far more effective than when dispersed by explosion from artillery shell. Speaking of the development, General Foulkes says:

> When the DA was scattered by the high explosive it was liberated not in the form of a gas, but in fine particles; these were not sufficiently minute to penetrate the gas mask completely, and absolute protection was very soon obtained by adding a cheesecloth filter to the canister.

Colonel Watson, who was the head of the Central Laboratory at Hesdin, had suggested in September 1917 the study of particulate clouds, and one of the officers in a spirit of investigation, put a pinch of DA which had been extracted from a German shell on the hot plate of a stove. The result was so remarkable that every one was driven out of the house immediately, and it was found that the latest pattern of German mask, even when fitted with a cheesecloth filter, gave no protection whatever against the DA cloud produced in this way.

This was the germ of a new and very valuable idea, and steps were taken immediately to investigate how DA could best be volatilized in the most highly effective and penetrant form by bringing it in contact with the heat evolved from the combination of a suitable mixture of chemicals; and a thermogenerator was soon designed, which consisted of a can containing the DA and the heating mixture in separate compartments and which weighed 2 or 3 lb.

The plan of attack was similar to the one previously put forward for gas; but as the particulate cloud was effective in one-hundredth the concentration of the gas cloud, and the German protection against it was nonexistent, complete success was absolutely certain if only the secret could be kept.

The "M" device (as the thermogenerators came to be called) was never used in France due to the termination of the war (15).

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15. Prentiss, op. cit., 209, 210.

CHAPTER II

Military Characteristics

Irritant Smokes

The desired characteristics of improved irritant smokes for use in shell are as follows:

1. When used in artillery shell it should be equal to or better than DM in the following:

   Rapidity of action.
   Effectiveness in low concentrations.
   Ability to penetrate the gas mask.
   Incapacitating effects.
   Stability during dissemination.

2. It should be effective in the field in the 75-mm. gun, the 155-mm. gun and howitzer, the 105-mm. howitzer, the infantry mortar, and the 4.2-in. chemical mortar.

3. It should be procurable in the quantities required in an emergency and stable in storage (16).

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16. "Revised Military Characteristics for War Gases," Minutes of the Chemical Corps Technical Committee (Army Chemical Center, Md.) CCTC Item 2288, 8 Mar 1951.

CHAPTER III

Basic Technical Factors

Preparation and Properties of Chlorodiphenylarsine

Preparation. Chlorodiphenylarsine was first observed by La Coste and Michaelis as a by-product in the preparation of dichlorophenylarsine from arsenic trichloride and mercury diphenyl according to the following equations:

$$Hg(C_6H_5)_2 + 2AsCl_3 \longrightarrow 2C_6H_5AsCl_2 + HgCl_2 \qquad (2)$$

$$Hg(C_6H_5)_2 + AsCl_3 \longrightarrow (C_6H_5)_2AsCl + HgCl_2 \qquad (3)$$

They then prepared it by heating mercury diphenyl with an excess of dichlorophenylarsine for several hours at a high temperature. The reaction is as follows:

$$2C_6H_5AsCl_2 + Hg(C_6H_5)_2 \longrightarrow 2(C_6H_5)_2AsCl + HgCl_2 \qquad (4)$$

Another method of preparation was to treat triphenylarsine, without a solvent, with dry chlorine gas, whereby the dichloro addition product was obtained. This latter product was then heated for some time at a high temperature and then distilled at reduced pressure. Chlorobenzene and chlorodiphenylarsine resulted. The reactions are as follows:

$$(C_6H_5)_3As + Cl_2 \longrightarrow (C_6H_5)_3AsCl_2 \qquad (5)$$

$$(C_6H_5)_3AsCl_2 \xrightarrow{\Delta} (C_6H_5)_2AsCl + C_6H_5Cl \qquad (6)$$

The same process has been reported by the French with the modification that the chlorination was carried out in chloroform or carbon tetrachloride solution. The yield of chlorodiphenylarsine was said to be 50% of theory. Richter, Byers, and Hunter used chlorobenzene as a solvent, following the French modification. The same authors report that triphenylarsine may be chlorinated by phosgene, the reaction being carried out in an ice bath.

A distinctly different process consisted in preparing diphenylarsenious oxide by the action of phenyl magnesium bromide on arsenious oxide, isolating the oxide, and treating it with hydrochloric acid to form chlorodiphenylarsine. The reactions are as follows:

$$As_2O_3 + 3C_6H_5MgBr \longrightarrow C_6H_5As(OMgBr)_2 + (C_6H_5)_2AsOMgBr \qquad (7)$$

$$2(C_6H_5)_2AsOMgBr \longrightarrow [(C_6H_5)_2As]_2O + MgBr_2 + MgO \qquad (8)$$

$$[(C_6H_5)_2As]_2O + 2HCl \longrightarrow 2(C_6H_5)_2AsCl + H_2O \qquad (9)$$

This process was developed and used as a laboratory method during World War I.

German Process. The German process carried out at Hochst-am-Main consisted in (1) preparing phenylarsonic acid by condensing benzene diazonium chloride with sodium arsinite, (2) reducing the acid with sulfur dioxide, (3) treating the resulting oxide with sodium hydroxide and condensing the product with benzene diazonium chloride to form diphenylarsinic acid, (4) reducing the arsinic acid to diphenylarsenious oxide, and (5) treating the oxide with hydrochloric acid to give chlorodiphenylarsine.

The entire process may be expressed by the following equations:

$$C_6H_5N_2Cl + Na_3AsO_3 \longrightarrow C_6H_5AsO_3Na_2 + NaCl + N_2 \quad (10)$$

$$C_6H_5AsO_3Na_2 + 2HCl \longrightarrow C_6H_5AsO(OH)_2 + 2NaCl \quad (11)$$

$$C_6H_5AsO(OH)_2 + SO_2 \longrightarrow C_6H_5AsO + H_2SO_4 \quad (12)$$

$$C_6H_5AsO + 2NaOH \longrightarrow C_6H_5AsO_2Na_2 \quad (13)$$

$$C_6H_5N_2Cl + C_6H_5AsO_2Na \longrightarrow (C_6H_5)_2AsO_2Na + NaCl + N_2 \quad (14)$$

$$(C_6H_5)_2AsO_2Na + HCl \longrightarrow (C_6H_5)_2AsO_2H + NaCl \quad (15)$$

$$2(C_6H_5)_2AsO_2H + 2SO_2 + H_2O \longrightarrow \left[(C_6H_5)_2As\right]_2O + 2H_2SO_4 \quad (16)$$

$$\left[(C_6H_5)_2As\right]_2O + 2\,HCl \longrightarrow 2(C_6H_5)_2AsCl + H_2O \quad (17)$$

The yield of chlorodiphenylarsine obtained by this method was 25% to 30% of the theoretical, based upon the aniline used (17).

The German process is conducted in four phases:

1st phase: The preparation of phenylarsenic acid. Into a solution of 420 kg. of calcined sodium carbonate in 2,500 kg. of water is poured a solution of 25 kg. of copper sulfate in 1,000 kg. of water; then a solution containing 560 kg. of arsenic acid (97-100%), 570 kg. of NaOH at 40° Bé., and 570 kg. of water is added. Then a solution of 400 kg. of aniline in 2,500 kg. of water and 350 kg. of 20° Bé. hydrochloric acid is prepared. After the addition of 1,350 kg. of ice with a solution at 40°C. of 742 kg. of sodium nitrate, the diazo solution is then diluted to 6,000 liters. The diazo solution is then

17. "Development of a Method for the Manufacture of Diphenylchloroarsine," EACD 259, pp. 2-3, 22 Mar 1923; W. LaCoste and A. Michaelis, "Uber aromatische Arsenverbindungen," Justus Liebigs Annalen der Chemie 201, p. 215, 219, 243 (1880); A. Michaelis, "Uber aromatische Arsenverbindungen," Ann. 321, pp. 142-148 (1902); W. LaCoste and A. Michaelis, "Uber Mono- und Diphenylarsenverbindungen," Berichte der Deutschen chemischen Gesellschaft, 11, p. 1885 (1878).

gradually added without going above 10°C. When the evolution of nitrogen has ceased, the solution is filtered and acidified by HCl. The precipitation of the phenylarsenic acid is aided to completion by the addition of sodium chloride, and filtered in a filter press.

Yield: 60% of the aniline used.

2nd phase: The preparation of phenylarsenic oxide. A mixture of 808 kg. of phenylarsenic acid, 800 kg. of water, and 1,500 kg. of a solution of bisulfite at 40° Bé. is heated at 90°C. until the reaction of the cuprous chloride no longer indicates the presence of phenylarsenic acid. The excess sulfur dioxide is driven off by steam, and the phenylarsenic oxide, which is deposited as an oil is dissolved in 700 to 750 kg. of 40° Bé. sodium hydroxide.

3rd phase: The preparation of diphenylarsenic acid. The alkaline solution of the phenylarsenic oxide is cooled by ice, then a diazo solution prepared from 325 kg. of aniline, 3,200 kg. of water, 1,040 kg. of 20° Bé. hydrochloric acid, and 620 kg. of sodium nitrite (in a 40% solution) is added. After the disappearance of the froth, 300 to 400 kg. of solution of sodium hydroxide is added, the resins are filtered, and the diphenylarsenic acid is precipitated by the addition of 1,000 kg. of hydrochloric acid. The yield is about 420 to 470 kg. (40 to 45% of the theoretical).

4th phase: The preparation of chlorodiphenylarsine. An introduction of 3,000 kg. of diphenylarsenic acid is made into 3,000 l. of preheated hydrochloric acid. Reduction takes place at 70°C. by the introduction of sulfur dioxide, and the chlorodiphenylarsine is precipitated. It is then dried under a low pressure by a current of air at the temperature of water bath (BM).

Yield: 90% of the diphenylarsenic acid used (18).

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18. "Combat Gases," Interallied Control Commission, Sub-Commission on Armament, Chemical Section for Control of War Factories, Office of Engineer of Powders, pp. 42-44 (undated). (In files of CRLTL as [illegible] 550, G-4.)

Green and Pope Process. The Green and Pope process is another method whereby chlorodiphenylarsine can be prepared. The first stages of the process are similar to the first stages of the German process. In the Green-Pope process, however, a part of the phenylarsenious oxide is converted to the corresponding chloride by treatments with hydrochloric acid, and a mixture of the two, in the proportion of three moles of phenylarsenious oxide to one mole of phenylarsenious chloride, is heated from one to two hours at 240° to 250°C.

The process may be expressed by the following equations:

$$C_6H_5N_2Cl + Na_3AsO_3 \longrightarrow C_6H_5AsO(ONa)_2 + N_2 + NaCl \qquad (18)$$

$$C_6H_5AsO(ONa)_2 + 2HCl \longrightarrow C_6H_5AsO(OH)_2 + 2NaCl \qquad (19)$$

$$C_6H_5AsO(OH)_2 + SO_2 \longrightarrow C_6H_5AsO_2 + H_2SO_4 \qquad (20)$$

$$C_6H_5AsO + 2HCl \longrightarrow C_6H_5AsCl + H_2O \qquad (21)$$

$$C_6H_5AsO \longrightarrow (C_6H_5)_3As + As_2O_3 \qquad (22)$$

$$(C_6H_5)_3As + C_6H_5AsCl_2 \longrightarrow 2(C_6H_5)_2AsCl \qquad (23)$$

The yield obtained by this method was 68% of theory, based upon the aniline used (19).

Based on the Green-Pope process a small-scale plant for the manufacture of DA was designed and constructed (20).

This pilot plant produced 1,637.5 lb. of crude DA in 34 runs over a period of six months of intermittent operation. The over-all yield of DA based on aniline was 30.2% of theoretical when hydrochloric acid was used throughout, but was increased to 42%, 61%, and 62% when sulfuric acid was used in the reduction step. A batch of the latter yielded about 80 lb. The estimated total cost in a plant producing 1 ton per 24-hr. day was given as $1.12 per lb. (21).

19. EACD 259, pp. 4-5.

20. "Design and Construction of a Small-Scale Plant for the Manufacture of Diphenylchloroarsine," EACD 298, 24 Nov 1923.

21. "The Development of the Manufacture of Diphenylchloroarsine (D.A.) on a Semi-Works Basis," EACD 225, p. 17, 8 Nov 1922.

Sodium Process. Adams and McDonall found that when mixtures of triphenylarsine and arsenic trichloride in theoretical proportions were heated at high temperatures in sealed tubes, the resulting product was largely chlorodiphenylarsine.

$$2(C_6H_5)_3As + AsCl_3 \longrightarrow 3(C_6H_5)_2AsCl \qquad (24)$$

Attempts were made to develop this process in a large-scale plant, both at the American University and in England using autoclaves (22).

The triphenylarsine was made from monochlorobenzene, arsenic trichloride, and metallic sodium, using benzene as a solvent and diluent. The method entailed the handling of large quantities of metallic sodium, which required careful plant construction and operation to guard against the danger of fire and explosions (23).

During fiscal year 1929, a plant for the production of DA by the sodium process was designed at Edgewood Arsenal and partially constructed (24).

The sodium for use in the reaction was prepared in two ways. In one process, the sodium was extended cold as a ribbon and cut in short lengths. In the other process, which consisted in forcing molten sodium through a small orifice into cold benzene, the sodium was obtained in a finely divided state, and the particles were fairly uniform in size.

Use of the theoretical quantity of sodium gave a yield of triphenylarsine as good as that obtained when an excess of sodium was used. The salt residue from the reaction could be destroyed by water without ignition of the residual benzene (25).

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22. "Preparation of Diphenylchloroarsine and Phenyl Dichloroarsine from Triphenylarsine and Arsenic Trichloride (Sealed Tube Method)," American University Experiment Station, Research Division, (Washington, D.C.), Offense Chemical Research Section Report (hereinafter O.R.) 23, 2 July 1918; "Report on the Manufacture of Diphenylchloroarsine," American University Experiment Station, Research Division, (Washington, D. C.), Chemical Production Section Report (C.P.) 20, 16 Aug. 1918.

23. "The Development of the Sodium Process for the Manufacture of Diphenylchloroarsine," EACD 434, 19 Oct. 1927.

24. "Manufacture of Chemicals for Experimental Purposes," Project Program for 1929-1930 (Chemical Warfare Service, Edgewood, Md.) Project Program F 12a, p. 43.

25. EACD 434.

Conversion of the crude triphenylarsine with a 25% excess of arsenic trichloride into chlorodiphenylarsine by heating 3 hr. at 250° to 255°C. under a pressure of 30 to 40 lb./sq.in., gave a product containing 64% to 68% chlorodiphenylarsine. The total recovery being 90% to 95% of the materials used. The materials cost per pound based on a typical laboratory run was 45 cents (26).

A total of 1,796 lb. of DA was manufactured, 1,239 lb. of which had a purity of approximately 92%. The calculated content of pure DA was 1,483 lb., which, based on the total arsenic trichloride used, corresponded to an over-all yield of 28.8%. It was estimated that a 64% over-all yield of pure DA could be obtained from a large-scale plant.

<u>Physical Properties</u> (27).

Molecular weight	264.57
Freezing point	
Stable form, °C.	37.3
Unstable form, °C.	18.2-18.4
Boiling point	
760 mm., °C.	307.2
in CO_2, °C.	333.
Decomposition temperature, °C.	300-350
Eballioscopic constant	38.7
Cryoscopic constant	44.55
Latent heat of vaporization, cal./g.	65.4
Latent heat of fusion, cal./g.	16.28
Heat of combustion, kg.-cal./mole.	1561
Heat of formation, kg.-cal./mole.	14.5
Specific heat at constant pressure at 20°C., cal./g.mole/degree.	0.270
Molar volume at 50°C., ml./g.mole.	190.7
Molar refraction for the sodium D line, ml./g.mole.	68.50
Coefficient of expansion	$10^4\alpha = 6.8$

26. "Chemical Warfare Agents," EATR 50, p. 50, 30 Jun 1931.

27. "Some Aspects of Physical Chemistry of War Gases," Chemical Defence Research and Development Monograph No. 9.311, p. 71, Sep. 1950, (In CRLTL as ETF 550 D-7736); "Constants and Physiological Action of Chemical Warfare Agents," EATR 78, p. 32, 33, 19 Jul 1932; "Diphenylcyanoarsine - Part V - The Physical Properties of MA, DA, TA, and DC," Chemical Defence Establishment (Sutton Oaks, England) Military Attache, Sutton Oaks Report (hereinafter S.O.R.) No. 492, p. 4-7, 4 Dec 1940.

Density, g./ml. . . . . $D^t = 1.4357-0.00097t$
Vapor pressure, mm.Hg. . . . . . . $\log p_t = 9.396-(\frac{3781}{T})$
Viscosity, g./cm.sec. or poise . . . . $\log \eta_t = (\frac{1000}{T}) - 4.466$
Refractive index with respect to air for the sodium D line... $n_D^t = 1.6663-0.00057t$

Temperature °C.	Density g./ml.	Vapor pressure mm.Hg.	Refractive index	Viscosity poise
20	1.4163	0.0016 (S)	1.6549	
30	1.4066			
40	1.3969		1.6435	
45		0.0032 (L)		0.0478
50	1.3872	0.0049	1.6376	0.0427
60	1.3775			
70	1.3678			
75		0.0684	1.6236	0.0292
80	1.3581			
90	1.3484			
100	1.3387	0.182	1.6093	0.0164
130		1.053		0.0105
150		—	1.5808	
165		5.808		0.0066
200		25.24	1.5523	0.0044
245		125.0		0.0029
307.2	1.1379	730.0	1.4913	

Solvent	Temp. 0°C.	Solvent g./100 g.
Benzene	15	108
Carbon tetrachloride	0° to Room temp.	Miscible
Ethanol	Room	20
Phosgene	25	495
Ethylene chloride	20	357
Chloroform	20.2	310
Dichloroethylene	19.5	337

Chemical Properties

Hydrolysis. DA is readily hydrolyzed by water or moist air to DA oxide.

$$2(C_6H_5)_2AsCl + H_2O \longrightarrow [(C_6H_5)_2As]_2O + 2HCl$$

The rapidity of hydrolysis depends on the subdivision of the DA and is increased by melting it in order to increase contact surface or shaking. The hydrolysis, when the mixture is agitated vigorously, is complete in 3 minutes at 40°C., and is 83% complete in 30 minutes at 20°C. (28).

Ammonia. With anhyrous ammonia and chlorodiphenylarsine in benzene solution, the following reaction takes place:

$$(C_6H_5)_2AsCl + 2NH_3 \longrightarrow (C_6H_5)_2AsNH_2 + NH_4Cl \qquad (25)$$

Diphenylarsenamide forms needles melting at 53°C. It acts on the skin and on the mucous membranes both in solution and when dispersed in the air. On exposure to air, it is converted into diphenylarsenious oxide.

Chlorine. By the action of a solution of chlorine in carbon tetrachloride on a solution of chlorodiphenylarsine in chloroform, trichlorodiphenylarsine is formed as crystals melting at 189°C.

$$(C_6H_5)_2As\begin{cases} Cl \\ Cl \\ Cl \end{cases} \qquad (26)$$

28. EATR 78, p. 35, 36; "Data on Chemical Warfare," Technical Division (Army Chemical Center, Maryland) Memorandum Report (Coordinator [illegible]) 456, 25 Nov 1942.

This trichloro-derivative on treatment with cold water forms first the chloride of diphenylarsenic acid:

$$(C_6H_5)_2AsCl_3 + 2H_2O \longrightarrow (C_6H_5)_2As(OH)_2Cl + 2HCl \qquad (27)$$

This is rapidly converted into diphenylarsenic acid.

Nitric Acid. Chlorodiphenylarsine on heating to about 40°C. with concentrated nitric acid is oxidized to diphenylarsenic acid, $(C_6H_5)_2AsOOH$. This forms colorless crystals melting at 175°C., which are sparingly soluble in hot water, alkalies, and alcohol. It is not decomposed by nitric acid nor by boiling chromic acid. The copper and lead salts of diphenylarsenic acid are very sparingly soluble in water, even at 100°C.

Hydrochloric Acid. On boiling chlorodiphenylarsine with hydrochloric acid, arsenic trichloride and triphenylarsine are formed as follows:

$$3(C_6H_5)_2AsCl \longrightarrow AsCl_3 + 2As(C_6H_5)_3 \qquad (28)$$

Sodium Iodide. By the action of sodium iodide on chlorodiphenylarsine dissolved in acetone, iododiphenylarsine is obtained:

$$(C_6H_5)_2AsCl + NaI \longrightarrow (C_6H_5)_2AsI + NaCl \qquad (29)$$

This forms brilliant yellow crystals, m.p. 40.5°C., insoluble in water, difficultly soluble in cold alcohol, but readily soluble in hot alcohol.

Hydrogen Sulfide. On bubbling hydrogen sulfide through an alcoholic solution of chlorodiphenylarsine, diphenylarsenious sulfide is formed:

$$2(C_6H_5)_2AsCl + H_2S \longrightarrow [(C_6H_5)_2As]_2S + 2HCl \qquad (30)$$

This forms white crystals melting at 67°C. It is readily soluble in benzene, carbon disulfide, and chloroform, but sparingly in alcohol and ether.

Sodium Thiocyanate. By the action of sodium thiocyanate dissolved in acetone on chlorodiphenylarsine dissolved in the same solvent, diphenylthiocyanoarsine is formed, $(C_6H_5)_2AsSCN$, an oily, pale brown substance which is miscible in all proportions with benzene and acetone and which decomposes with water, giving up the SCN group. It boils at 230° to 233°C. at 22 to 23 mm.Hg. pressure. It reacts quantitatively with sodium sulfide.

$$2(C_6H_5)_2AsSCN + Na_2S \longrightarrow [(C_6H_5)_2As]_2S + 2NaSCN \qquad (31)$$

Sodium Alcoholate or Phenate. Sodium alcoholate and phenate react with chlorodiphenylarsine as follows:

$$(C_6H_5)_2AsCl + C_2H_5ONa \rightarrow (C_6H_5)_2AsO.C_2H_5 + NaCl \quad (32)$$

$$(C_6H_5)_2AsCl + C_6H_5ONa \rightarrow (C_6H_5)_2AsO.C_6H_5 + NaCl \quad (33)$$

Chloramine-T. Chlorodiphenylarsine reacts with chloramine-T in the presence of water to form diphenylarsenic acid (29).

Corrosion Characteristics. The pure substance has no corrosive effect since it is stable. When wet the acid hydrolysis product is corrosive to metals.

Stability in Storage at 25° and 60°C. DA can be kept in steel shell for at least 15 wk. at 60°C. and for a year at room temperature, without deterioration of the toxic or the shell (30).

Preparation and Properties of Cyanodiphenylarsine

Preparation.

DC Process, Sodium Cyanide Method. During World War I cyanodiphenylarsine was prepared in Germany by heating potassium cyanide with chlorodiphenylarsine.

$$(C_6H_5)_2AsCl + KCN \longrightarrow (C_6H_5)_2AsCN + KCl \quad (34)$$

A 5% excess of a concentrated aqueous solution was used.

This method was investigated by the Lake Erie Chemical Co., Cleveland, Ohio, between 1936 and 1941, as well as at Edgewood Arsenal in 1932, and it was found that emulsion formation was caused by the rapid hydrolysis of DA by the alkaline sodium cyanide.

Moreover, any dichlorophenylarsine present is hydrolyzed to the oxide. This is the very vigorous and exothermic reaction that makes it difficult to maintain a low temperature, (30°C.) which was found to be advantageous and increases the emulsion formation.

$$C_6H_5AsCl_2 + 2NaCN \longrightarrow C_6H_5As(CN)_2 + 2NaCl \quad (35)$$

$$C_6H_5As(CN)_2 + H_2O \longrightarrow C_6H_5AsO + 2HCN \quad (36)$$

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29. Mario Sartori, The War Gases (New York: D. Van Nostrand Company, Inc.), p. 310, 311, 312.

30. EATR 78, p. 36

The quality of the DA used was a great importance, but only when the purity of DA was above 95% could emulsion formation be consistently prevented. The conversion in all cases was about 90%.

DC Process, Aqueous Oxide Method. The method of manufacture recommended by the Lake Erie Chemical Company consists of hydrolyzing DA with aqueous sodium hydroxide to form DA oxide.

$$2(C_6H_5)_2AsCl + 2NaOH \longrightarrow [(C_6H_5)_2As]_2O + 2NaCl + H_2O \qquad (37)$$

In this method any arsenic trichloride is reacted with sodium hydroxide to form water-soluble sodium arsenite.

$$AsCl_3 + 6NaOH \longrightarrow Na_3AsO_3 + 3NaCl + 3H_2O \qquad (38)$$

In a similar fashion, the impurity dichlorophenylarsine hydrolyzes to water-soluble products.

$$C_6H_5AsCl_2 + 2NaOH \longrightarrow C_6H_5AsO + 2NaCl + H_2O \qquad (39)$$

$$C_6H_5AsO + 2NaOH \longrightarrow C_6H_5As(ONa)_2 + H_2O \qquad (40)$$

The diphenylarsenious oxide, which is insoluble in water, can be filtered from the water-soluble impurities. It is converted to DC by suspending it in water and passing in HCN to form DC.

$$[(C_6H_5)_2As]_2O + 2HCN \longrightarrow 2(C_6H_5)_2AsCN + H_2O \qquad (41)$$

The DC obtained by the aqueous oxide method has a purity of better than 98% after separation of the DC layer and vacuum drying (31).

Physical Properties (32).

Molecular weight	255.13
Molar volume at 20°C., ml./g.mole	193.4

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31. "Manufacturing Process for Diphenylcyanoarsine Including Diphenylchloroarsine and Triphenylarsine." Lake Erie Chemical Company, (Cleveland, Ohio.), Report No. 6120, 9 Dec 1941. (In CRLTL as ETF 102C3-6.)

32. "Physical Constants of Arsenicals Related to DC," Chemical Experimental Station (Porton, England), Porton Report (hereinafter, P.R.) 2272, p. 5-6, 10 Sep 1941; S.O.R. 492, p. 7-9; ETF 530 E-7736, p. 73.

Molar refraction for the sodium D line, ... 67.26
ml./g.mole 290.4
Boiling point, °C. 30.0
Freezing point, °C. 28.95 ± 0.15
metastable isomorphs, °C. 79.3
Latent heat of vaporization, cal./g. 31.2
Eballioscopic constant 0.315
Specific heat at constant pressure at 20°C., cal./g. . . . . .

Temp. °C.	Vapor Pressure mm.	Density g./ml.	Refractive Index N_D	Viscosity poise
33.3	—	—	1.6239	—
35	—	1.3338	1.6231	0.098
45	—	1.3234	—	0.073
52	—	—	1.6153	0.060
55	—	1.3143	1.6131	0.056
65	—	1.3048	1.6081	0.043
75	—	1.2955	1.6031	0.034
160	2.0	1.2148	1.5606	—
180	4.5	—	—	—
190	7.5	1.1863	1.5468	—
210	18.0	1.1673	1.5358	—
229	38.5	—	—	—
240	50.5	1.1388	1.5208	—

This data was obtained from the following formulas:

Vapor pressure, mm.Hg. $= 10.724 - \left(\frac{4420}{T}\right) = \log P_t$

Density, g./ml. $= 1.3668 - 0.00095t$

Refractive index $= 1.6406 - 0.00050t$

Viscosity, poise $= \left(\frac{1240}{T}\right) - 5.035 = \log \eta_t$

Chemical Properties.

Hydrolysis. Cyanodiphenylarsine is less easily hydrolyzed by water than DA. A 50% mixture of DC and water showed no hydrolysis after 24 hr. either at 60°C. or at 80°C. At temperatures higher than 80°C., the decomposition was rapid and was complete at 100°C. This decomposition takes place more rapidly with aqueous or alcoholic solutions of the alkalies (33).

Oxidizing Agents. When cyanodiphenylarsine, cooled in a water bath, is treated with nitric acid, with 2% hydrogen peroxide, or with bromine water, it is oxidized to diphenylarsenic acid.

Methyl Iodide. By the action of methyl iodide on cyanodiphenylarsine, through heating in a closed tube for 6 hr. at 100°C., diphenylmethylarsonium iodide and triiodide are obtained. The latter crystallizes in violet needles which melt at 69°C. and are insoluble in water and in ether (34).

Thermal Stability. No change in composition occurred on heating DC for 105 hr. at 65°C. or for 58 hr. at 80°C. (35).

Preparation and Properties of Diphenylaminechloroarsine

Preparation. Wieland obtained DM by treating diphenylamine with arsenic trichloride:

$$(C_6H_5)_2NH + AsCl_3 \longrightarrow NH(C_6H_5)_2AsCl + 2HCl \qquad (42)$$

It can also be obtained by the following methods:

1. By heating diphenyl hydrazine with arsenic trichloride.

2. By boiling aniline with arsenic trichloride, then adding sodium hydroxide, and treating the oxide obtained with hydrochloric acid.

3. By treatment of fused diphenylamine with concentrated hydrochloric acid and then mixing with arsenious oxide.

$$(C_6H_5)_2NH + HCl \longrightarrow (C_6H_5)_2NH \cdot HCl \qquad (43)$$

$$2(C_6H_5)_2NH \cdot HCl + As_2O_3 \longrightarrow 2NH(C_6H_4)_2AsCl + 3H_2O \qquad (44)$$

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33. ETF 102C3-6, p. 54-55

34. Mario Sartori, op cit. p. 317

35. ETF 102C3-6, p. 53

The manufacturing process used by the Americans at Edgewood Arsenal during orld War I for the manufacture of DM was based on the reaction of diphenylamine ith arsenic trichloride.

The operating details of the method were as follows:

> In a large jacketed kettle fitted with an agitator and a reflux condenser 642 kg. of diphenylamine was heated to 150°C. To this was added 730 kg. of arsenic trichloride (10% excess over theoretical), and the heating was continued for 5 hr. During the course of the reaction, the temperature rose to 250°C., and large quantities of hydrogen chloride were evolved. This passed through the condenser and was absorbed in water in a special absorption tower. At the end of the reaction, the product obtained was transferred to a vessel containing water where it was washed, centrifuged, and dried at 30°C. The yield was 80% of theory (36).

In the plant 8,183 lb. of DM were manufactured by this method. The cost of production was $0.95 per lb. of DM.

Physical Properties (37).

Molecular weight	277.57
Molar volume at 20°C., ml./g.mole.	168.4
Boiling point, °C., 760 mm. Hg	401 (British) 410 (American)
Ebullioscopic constant	59.4 (British)
Freezing point, °C.	195
unstable forms, °C.	182 and 186
Cryoscopic constant	48.4
Decomposition temperature, °C.	195
at 200°C. decomposition	0.02% per min.
at 250°C. decomposition	0.15% per min.
Specific heat (solid), cal./g.	0.222 (American) 0.270 (British)
Latent heat of vaporization, cal./g.	51.0 at 410°C. (American) 80.1 from 200-250°C. (American)
Latent heat of fusion, cal./g.	79.3 at 195°C. (American)
Latent heat of sublimation, cal./g.	159.4 (American)

36. Mario Sartori op. cit., p. 320, 321.

37. ETF 550 E-7736, p. 74; EATR 78, p. 26-28; "Vapor Pressure of D.M." EACD 46, 1 Jun 1921; "Report on Improvement of the Existing D.M. Generator," P.R. 417, Part I, Nov 1926.

Temp. °C.	Vapor pressure mm. Hg	Volatility mg./l.	Density g./ml.
0	5×10^{-16} (A)	8.15×10^{-15} (A)	1.672
20	2×10^{-13}	3.0×10^{-12}	1.648
40	3×10^{-11}	4.3×10^{-10}	1.624
60	2×10^{-9}	2.6×10^{-8}	1.600
100	2×10^{-6}	2.4×10^{-5}	1.552
140	8×10^{-4}	8.62×10^{-3}	1.504
195	0.43	2.089	1.438
216	1.0 (B)	—	—
220	1.38	12.42	
242	3	—	—
303	23	—	—
328	48	—	—
340	117	849.	—
362	108	—	—
378	258	—	—
391	578	—	—
400	750	—	—
410	760	4,968.	—

(A) American Data

(B) British Data

Density was calculated from the following equation:

$$d_t = 1.672 - 0.0012t.$$

Much doubt still prevails concerning the vapor pressure of Adamsite. British results, P.R. 417, obtained in the region 240° to 400°C., and American results, EACD 46, obtained in the region 140° to 410°C., are not only contradictory, but internally inconsistent. Although it is somewhat difficult to judge, the discrepancies appear to be due less to impurity in the specimens than to the inherent difficulties of measurement (38).

Solvent	Temp. °C.	Solubility g./100 g.
Ethylene chloride	0	0.32
Ethylene chloride	60	2.8
Chloroform	20	<0.87
Dichlorethylene	40	<3.2
Tetrachlorethane	20-25	<2.91
Carbon disulfide	20-25	<0.[illegible]
Pyridine	40	About 7
Monochloroacetone	25-28	8.2
Chloropicrin	40	<0.35
Acetone	Room temp.	20

Chemical Properties.

Hydrolysis. When DM is covered with water it probably forms a protective coating of DM oxide which prevents further hydrolysis. Finely divided DM hydrolyzes rapidly, to the extent of about 30% in 15 min. and 40% in 1 hr. Increase in temperature and time of contact seem to have no effect on hydrolysis.

At room temperature a concentration of 0.5% hydrochloric acid is sufficient to prevent hydrolysis, and at 70° to 80°C., a concentration of 0.8% is required (39).

38. ETF 5£0 E-7736, p. 14.

39. EATR 78, p. 29.

The hydrolysis is probably

$$2NH(C_6H_4)_2AsCl + HOH \longrightarrow \left[(NH(C_6H_4)_2As\right]_2O + 2HCl \qquad (45)$$

Bromine. By the action of bromine on DM in acetic acid solution, the molecule is decomposed, and tetrabromodiphenylamine is formed:

$$HN\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}AsCl + 4Br_2 \longrightarrow HN(C_6H_3Br_2)_2 + AsBr_3 + HCl + HBr \qquad (45)$$

Tetrabromodiphenylamine forms lustrous crystals melting at 185° to 186°C.

Hydrochloric Acid. When DM is treated with gaseous hydrochloric acid at 160°C., it decomposes, forming arsenic trichloride and diphenylamine, as follows:

$$NH\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}AsCl + 2HCl \longrightarrow NH(C_6H_5)_2 + AsCl_3 \qquad (47)$$

Hydriodic Acid. On treatment with aqueous hydriodic acid on the water bath, DM forms diphenylamine:

$$NH\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}AsCl + 2HI \longrightarrow NH(C_6H_5)_2 + AsClI_2 \qquad (48)$$

Alkalies. DM reacts with alkalies to form DM oxide, according to the following equation:

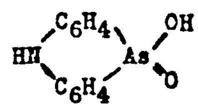
$$2NH\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}AsCl + H_2O \longrightarrow 2HCl + \left(HN\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}As\right)_2O \qquad (49)$$

This substance forms colorless leaflets with a melting point above 350°C. and is soluble with difficulty in most of the organic solvents.

Ammonia. When a current of dry ammonia is passed through a solution of DM in xylene, triphenarsazine amine, melting at 295° to 300°C., is obtained.

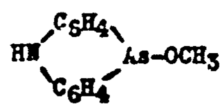
$$\left(HN\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}As\right)_3N \qquad (50)$$

Oxidizing Agents. Oxidizing agents react with DM, converting the arsenic atom from the trivalent to the pentavalent state. Hydrogen peroxide in acetic acid solution, or chloramine T in cold aqueous alcoholic solution, converts DM to phenarsazinic acid, melting above 300°C.



(51)

Cyanides. DM, when treated with sodium cyanide in methyl alcohol solution, does not form DM cyanide, but the corresponding methoxy compound.

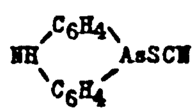


(52)

This substance melts at 194°C. and on heating with water is converted to DM oxide.

DM cyanide has been prepared by treating DM with silver cyanide. It forms bright yellow crystals melting at 227°C. Though it has a more efficient biological action than DC, it is very unstable to heating and to explosion.

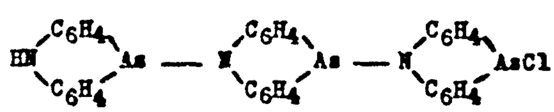
Potassium Thiocyanate. When DM is treated in acetone solution with an aqueous solution of potassium thiocyanate, DM thiocyanate is formed.



(53)

This forms yellow crystals which melt at 229° to 230°C.

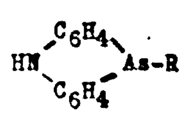
Pyridine. When DM is treated with boiling anhydrous pyridine, triphenarsazine chloride is formed.



(54)

The compound is orange yellow and melts at 260° to 263°C.

Grignard Reagent. By the action of the Grignard reagent on DM the corresponding alkyl or aryl derivative is formed (40).



(55)

40. Mario Sartori, Op Cit, p. 323-326.

Corrosion Characteristics. When stored in steel shell, DM causes a slight rusting due to the small amount of acid present as arsenic trichloride.

Stability in Storage at 25° and 60°C. DM may be stored in steel shell for 15 wk. at 60°C. or for a year at room temperature without deterioration, or without any appreciable effect on the shell (41).

Theory of Smoke Formation

There are three ways in which smokes can be produced. These are:

1. Condensation of a supersaturated vapor.
2. Atomization of a liquid.
3. Pulverization of a solid.

Condensation of a Supersaturated Vapor. The condensation of a supersaturated vapor results in a smoke. This method can be carried out in a number of ways: by heating, by chemical interaction, and by adiabatic expansion. Since the starting unit is the molecule, this method is extremely efficient in obtaining small particles providing the growth can be arrested. However, it is very difficult to stop this growth, since condensation, once begun, proceeds continuously until the state of supersaturation disappears. The fewer number of particles formed initially, the greater is the growth of particle size. Small particles can be obtained by supplying a large number of nuclei for the condensation of smoke molecules.

Atomization of a Liquid. Atomization can be applied only to liquids. When a shell containing a liquid is exploded, the impact of the gas of explosion upon the liquid, combined with the impact of the liquid upon the surrounding atmosphere, tends to stretch the liquid into a thin film. When a liquid is suddenly stretched in a thin film, its surface is enormously extended until the resulting tension exceeds the surface tension of the liquid. At this point the film breaks up into numerous small spherical droplets whose total surface is less than that of the film, and therefore in a more stable state. The degree of dispersion obtained will depend upon the speed with which the process can be carried out, which in turn is a function of the velocity of impact and of the viscosity of the liquid. If the velocity of impact travels faster than the liquid can be formed into droplets, the liquid will fall to the ground in large drops. Increased viscosity delays the extension of the surface, thus tending to cause the formation of large aggregates.

Since relatively a much greater amount of energy will be required to atomize

41. EATR 78, p. 30.

iquid of high viscosity, much greater pressures are required in a shell to ain a given degree of dispersion if the liquid filling is very viscous.

The lower the surface tension of the liquid, the less will be the amount of rgy required to extend the liquid, and therefore, other things being equal, further the surface is extended for a given impact, the finer the smoke will Since the limiting factor in the thickness of the film is the surface sion, the minimum particle size that can be obtained for a given liquid ardless of how much energy is expended, will depend upon this property.

High density is another retarding factor, and the lower the density of a uid the further it will be extended by a given impact.

The degree of dispersion that can be produced with a given expenditure of rgy by explosion of a shell can be increased by reducing the viscosity ising the temperature), by lowering the surface tension, and by increasing velocity of impact.

Explosive Disruption of a Solid. In the disintegration of a solid it is essary to overcome large forces of cohesion, and the amount of energy reired will be proportional to the specific surface of the powdered material. is important to notice that in whatever way this work of disintegration is ne, the energy that is expended appears as heat. In the majority of cases is heating effect is great enough so that where the velocity of impact is gh, as in explosive disruption, the particles are fused together after the terial is fractured, thus decreasing the degree of dispersion. If the impact violent enough, liquifaction will take place.

The efficiency with which a solid can be dispersed in the form of a smoke explosive means, provided the material does not fuse, depends on the rigidity the material acted on and the velocity of impact. In all detonation processes e limit of disintegration is reached when the fractured material is fine ough to accomodate itself to the applied stress without the individual articles actually being stressed beyond their elastic limit. When a stress is pplied slowly, the forces of cohesion absorb the energy of the stress before t can travel far. The velocity of impact must be such that the rate at which he stress is applied exceeds the rate of deformation. It is evident then that nly those solids whose melting points are higher than the temperature which he individual particles would attain are capable of being efficiently dispersed. If the solid was liquified during the impact, then the process of atomization of liquid would take place (42).

42. EATR 286, pp. 18-20.

CHAPTER IV

Design Characteristics

Development Work on Irritant Smoke Shell (1933-1942)

A research program was started at Edgewood Arsenal in 1933 to develop an irritant smoke suitable for use in the field, especially by artillery dispersion. A series of tests were carried out on 75-mm. smoke shell filled with DM, DA, and DC. A comparison of the best DM, DA, and DC shell tested are given in the following table:

Comparison of DM, DA, and DC

	DM	DA	DC
Designation of best shell tested	E1R9	E3R5	E4R1
Type	Mixture	Long burster	Long burster
Wt. TNT in shell, g.	130	248	108
Wt. agent in shell, g.	392	388	476
Wt. of unchanged agent in smoke, g.	21.1	33.1	27.0
Wt. of agent converted to other as compound in smoke, g.	77.3	10.5	337.7
Wt. of agent not appearing as smoke, g.	293.6	344.4	111.3
Total, g.	392.0	388.0	476.0

DM Shell. The best DM shell tested was the E1R9 consisting of the following components:

Shell body	-	75-mm. Mk.II
Fuze	-	PD Mk.III
Adapter and booster	-	MK IVB
Filling	-	541 ± 10 g. of a mixture containing 75% flake DM and 25% TNT.

The shell was filled by hand tamping and drilling a hole in the mixture to permit the booster to descend upon closing the shell.

In this shell 25.1% of the DM in the shell, or 98.4 g., was disseminated as a smoke, which analyzed 21.3% DM. However, in the analysis of DM it was found impossible to distinguish between DM and certain decomposition products of DM, and since these decomposition products had a very low irritating effect, it appeared very probable that the product in the smoke listed as DM contained some of these nonirritating substances. This was borne out by the slight incapacitating effects of the smoke during field tests, and nonpenetration of the MVIII canister during the chamber tests. The fragmentation was considered to be good, but not equal to the HE shell, as is shown in fig. 1.

DA Shell. The best DA shell tested was the E3R5, consisting of the following components:

Shell body	-	75-mm. MK. I HE
Fuze	-	M46
Adapter and booster	-	Seamless steel tube 1-3/8 in. o.d., 20-gage, 9-1/4 in. long, welded to adapter.
Filling	-	DA, 388 ± 5 g.

This shell was almost identical with type L toxic smoke shell for dispersion of DA, of which 200 were fired at Lakehurst Proving Ground in 1918. The burster was loaded by filling the tube with melted TNT, using a riser to eliminate a hollow center. After cooling, a hole was drilled in the TNT to take the tetryl pellets, which were the same as those used in the Mk. IVB booster. The weight of the TNT was 248 ± 5 g. Filling, 388 ± 5 g. DA (purity 85.5%). The liquid DA was measured into the shell (allowing 10% void) and the burster screwed in by hand until it was securely bottomed. The shell was sealed by means of a lead washer and lock nut.

The amount of DA disseminated as a fine smoke when the E3R5 shell was tested was 11.3%. The bulk of the agent was atomized as a coarse mist which settled out very rapidly. In chamber tests, the MVIII canister was slightly penetrated. The fragmentation was considered equal to that of the HE shell and is shown in fig. 2.

DC Shell. The best DC shell tested was the E14R1, consisting of the following components:

Shell body	-	75-mm. Mk.I, HE
Fuze	-	M46
Adapter and booster	-	Seamless steel tube, 1-1/16 in. o.d., 16-gage, 9-1/4 in. long, welded to adapter
Filling	-	DC, 476 ± 5 g.

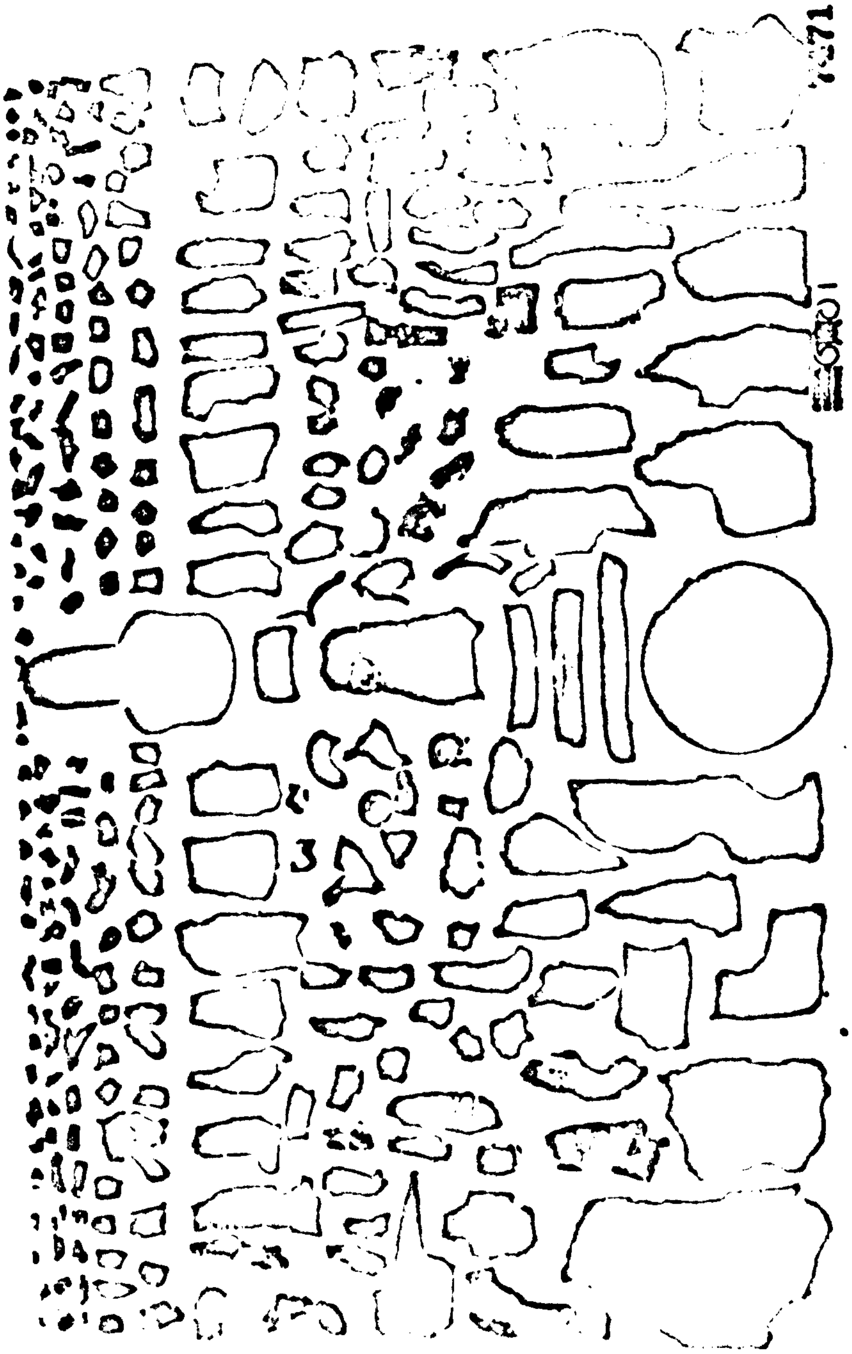


Figure 1. -FRAGMENTATION OF E1R9 75-MM. SHELL

Figure 2.--FRAGMENTATION OF E3R5 75-MM. SHELL

The burster was loaded by filling the tube with melted TNT, using a riser to eliminate a hollow center. After cooling, a hole was drilled in the TNT to take the tetryl pellets, which were the same as those used in the Mk.IVB booster. The weight of TNT was 108 + 5 g. Filling 476 + 5 g. DC (purity 96.3%). The liquid DC was measured into the shell (allowing 10% void) and the burster screwed in by hand until it was securely bottomed. The shell was sealed by means of a lead washer and lock nut.

When the DC shell were tested in the dispersion chamber, some remarkable results were observed. The tests in the chamber showed that in most cases a large part of the DC was burnt during the explosion, and that one of the products of combustion was a very fine smoke made up mainly of arsenic trioxide. This smoke was found to be very irritating and could readily penetrate the MVIII canister to cause severe irritation. The same shell when tested in the field did not behave the same way, and the resulting smoke obtained contained no arsenic trioxide.

This burning could not be controlled, and was traced to the initial ignition of the hydrocyanic acid liberated by the DC during the explosion. The field tests showed no such combustion taking place. Several suggestions were made as to how to effect this combustion when the shell are fired in the open. One way would be to add a combustible substance to the agent to cause it to flash upon explosion. Another way would be to use an agent which itself is spontaneously combustible, or highly inflammable, and whose products of combustion would be highly irritating or toxic. Such a substance might be found among the cacodyl compounds. Many of these readily inflame in air, giving rise to arsenic trioxide fumes, the same substance resulting from the burning of DC. The possibility was considered of using mixtures of these cacodyl compounds with DA or similar irritants to decrease the hazards in loading or increase the irritating properties of the smoke. The best line of attack to increase the smoke concentration of the 75-mm. irritant smoke shell appeared to be the use of cacodyl compounds such as cacodyl, $(CH_3)_2As\text{-}As(CH_3)_2$ by itself, or in mixtures. In a conference of the American Chemical Society Advisory Committee, 21 October 1938, during the discussion of project A 2, the members of all concurred in the opinion that cacodyl compounds offered very promising leads (43).

Mixtures of Cacodyl and DC. A series of tests were conducted in which DC was mixed with cacodyl in a 75-mm. and 105-mm. shell containing a long burster filled with TNT. The effect of the addition of cacodyl was presumed to be as follows:

The initial explosion of the shell, due to the TNT, sprays out the liquid contents of the shell in a fine spray or mist along with a small amount of smoke. The fine droplets of the mixture normally would settle out quickly, but as soon as the mixture comes in contact with the air, the cacodyl begins to react with the oxygen of the air, liberating heat, and resulting in the formation of arsenic trioxide smoke. The resultant heat vaporizes

43. "Irritant Smoke. DM, DA, and Cyan-DA in 75-Mm. Shell, Status Report on Engineering Tests Under Project A2", EATR 308, p. 48, 29 Nov 1939.

The burster was loaded by filling the tube with melted TNT, using a riser to eliminate a hollow center. After cooling, a hole was drilled in the TNT to take the tetryl pellets, which were the same as those used in the Mk.IVB booster. The weight of TNT was 108 + 5 g. Filling 476 + 5 g. DC (purity 96.3%). The liquid DC was measured into the shell (allowing 10% void) and the burster screwed in by hand until it was securely bottomed. The shell was sealed by means of a lead washer and lock nut.

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43. "Irri[illegible] Smoke. [illegible], DA, and Cyan-DA in 75-Mm. Shell, Status Report on Engineering Tests Under Project A2", EATR 303, p. 48, 29 Nov 1939.

the DC, which immediatly condenses into a smoke. If the oxidation of the cacodyl becomes too rapid, a flash results, and part of the DC also burns, and the yield of DC smoke will decrease.

It was found that with the 75-mm. shell the best of those tested was the E8R1, consisting of the following components:

Shell body	-	75-mm. Mk.I HE
Fuse	-	M46
Adapter and burster	-	Seamless steel tube 1-1/8 in. o.d., 16-gage, 9-1/4 in. long, welded to adapter.
Explosive charge	-	119 ± 8 g. TNT, 34.5 g. tetryl
Filling	-	DC, 250 ± 2 g.
		Cacodyl, 224 ± 6 g.

The average smoke cloud from these shell in the dispersion chamber contained irritant arsenicals equivalent to 118 g. of DC or 47.1% of the DC in the shell.

The smoke set up in the chamber was very irritating and could readily penetrate the M1XA1 canister to cause severe irritation. The results of the field tests showed that the shell functions equally as well as in the chamber.

The toxicity of the smoke was of the same order of magnitude as that of the most toxic agents (44).

Four field tests were conducted to determine the best mixture of DC and cacodyl to use in 105-mm. projectiles fired statically in the open. The fillings were composed of 42.6%, 44.1%, 45.1%, and 47.2% cacodyl, the remainder being DC.

With 42.6% of cacodyl, a poor cloud was obtained that did not penetrate the M1XA1 canisters. With 44.1% cacodyl, a very dense cloud was obtained, and there was evidence of canister penetration. With 45.1% cacodyl, a very dense cloud was obtained that could penetrate the masks of some of the observers. With 47.2% cacodyl, a dense cloud was obtained, but analysis showed a low percentage of trivalent organic arsenic in the smoke. There was some evidence of canister penetration.

The optimum amount of cacodyl was thus 44.1% to 45.4% in a 105-mm. shell when fired statically (45).

44. "Gas (2) for Navy HE-Gas Projectiles. Dispersion of Mixtures of Cyan DA and Cacodyl in 75-Mm. Shell," TDMR 288, 2 June 1941.

45. "Gas (2) for Navy HE-Gas Projectiles. Dispersion of Mixtures of Cyan DA and Cacodyl in 105-Mm. Projectiles in the Open," TDMR 357, 10 Feb 1943.

On the basis of these results a field test was conducted in which a battery of 105-mm. howitzers fired modified M60 projectiles (E2), containing cacodyl and DC, on an artillery square at combat rate. The filling consisted of 44.85% cacodyl and 55.15% DC. The analysis of the smoke indicated too much oxidation and that the filling should have consisted of 43% cacodyl and 57% DC (46).

Mixtures of Cacodyl and DA. Since the use of cacodyl in dispersing DC from 75-mm. projectiles was satisfactory, tests were run to determine whether DA could be dispersed equally as well. The DA-cacodyl considered to be the best of those tested, was the E10R1, consisting of the following components:

Shell body	-	75-mm. Mk.I HE
Fuze	-	M46
Adapter and Burster	-	Seamless steel tube, 1-1/8 in. o.d., 16-gage, 9-1/4 in. long, welded to adapter.
Explosive charge	-	130 g. TNT, 32.7 g. tetryl
Filling	-	258 g. DA, 236 g. cacodyl

The smoke cloud from this projectile in the dispersion chamber contained 73.67 g. of DA or 28.5% of the DA in the projectile.

The smoke set up by the DA-cacodyl-filled projectile was highly toxic and irritating and penetrated the M1XA1 canister in the chamber tests, but the penetration was not as well as that obtained from the DC-cacodyl-filled projectile (47).

Toxic Smoke Candle (1920-1942)

Development of Candle, Gas, Irritant, DM, M2. From an energy standpoint thermal dispersion is not very efficient when applied to a shell, as the heat required to vaporize the smoke-producing material is usually large, and the explosives used do not have a sufficiently large energy content. Explosives, such as TNT, are valuable because they liberate all their energy in a very short space of time, but the amount of energy liberated is not very high. Thus 1 kg. of petroleum has a heat of combustion of about 12,000 cal., coal about 8,000, and dry wood 3,500 to 4,000, while TNT in exploding has only 710

46. "Gas (2) for Navy HE-Gas Projectiles. Modified M60 105-Mm. Projectiles Filled With a Mixture of Cyan DA and Cacodyl Impact Field Test of March 1, 1942," TDMR 363, 6 Apr 1942.

47. "Gas (2) for Navy HE-Gas Projectile. Dispersion of Mixtures of DA and Cacodyl in 75-Mm. Projectile," TDMR 365, 29 Apr 1942.

cal. Explosives are inefficient and costly sources of energy, especially when used for heating purposes.

The "M" Device developed by the British during World War I was designed to overcome the inefficiency of the explosive shell in generating toxic smoke. It consisted of a can containing DA and the heating mixture in separate compartments. In operation the heating mixture was ignited, and the heat developed in burning volatilized the toxic agent, which condensed to form a smoke which was far more effective than when dispersed by explosion from artillery shell.

From 1920 to 1922 a considerable amount of work was done on finding a suitable fuel for dispersing DM. Three types of fuels were investigated:

1. Type 1 fuels depended upon air to supply oxygen for combustion. Due to the unsatisfactory nature of this type of design, the fuels which were mainly solidified alcohols, were not considered suitable.

2. Type 2 fuels produced a large amount of heat and deposited a hot slag which retained its heat long enough to volatilize the agent. In addition, it was found desirable that the fuel liberate a minimum of gaseous products, since these hot gases caused explosions.

For the Type 2 candle the following were considered the most satisfactory:

<u>No. 15</u>

Potassium permanganate	53%
Iron	47%

<u>No. 40</u>

Iron	30.2%
Zinc	35.2%
Sulfur	34.6%

<u>No. 106</u>

Daisite (mixture of aluminum, magnetic iron ioxide, sulfur)	60%
Sand	40%

These fuels were similar in behavior since they burned uniformly with little or no flame, forming only a small amount of gaseous products from the reaction and a good hard slag, capable of holding its volume nearly constant and retaining its heat long enough to volatilize the agent.

3. Type 3 fuels gave off a large volume of nonreactive gas at a moderately low temperature. The oxygen required for the combustion was combined with the fuel. The best fuels for the Type 3 candle were found to be either smokeless powder or a mixture of ammonium nitrate and charcoal. The smokeless powder fuel consisted of 12-in. powder, which was placed in an upright position, and sufficient cal. .30 smokeless powder to fill the void spaces between the 12-in. powder. The entire mass was gelatinized by means of a solution of 1 part of alcohol and 2 parts of ether. The ammonium nitrate fuel consisted of a mixture of 85% ammonium nitrate and 15% charcoal. This mixture was pressed into a cake using a pressure of 500 to 750 lb. The ammonium nitrate fuel proved as efficient as the smokeless powder fuel for the evolution of DM.

The fuel used in the DM irritant candle M1 consisted of a mixture of 2.75 lb. of the 12-in. cannon powder and approximately 0.5 lb. of cal. .30. service ammunition powder to fill the void spaces between the large grains of powder completely. The two types of powder were consolidated by adding a solvent of alcohol and ether, and then evaporating off the solvent from the plastic mass.

The burning time of the DM irritant candle M1 was between 2.5 and 5 min. (48).

The DM irritant candle M2, which was developed in 1941 contained the following fuel:

	Percent
Ammonium nitrate	68.0 ± 0.5
Ammonium chloride	7.0 ± 0.25
Calcium carbonate	12.0 ± 0.25
Charcoal	13.0 ± 0.25

The mixture was mixed with a 4% solution of collodion in acetone and pressed into the fuel compartment of the candle.

This fuel was merely a substitute for the fuel in the M1 candle. It did not result in any better dispersion of the DM (49).

48. "New Methods of Dispersing Chemical Agents, Low Temperature Fuels for Generating Toxic Smokes," TDMR 214, pp. 2-3, 5, 13 Feb 1940; "9-Pound D.M. Candle," EACD 7[illegible], p. 57, 1 Feb 1924.

49. "Development of a New Fuel for the DM Candle," TDMR 479, 5 Dec 1942.

Comings Candle. In 1942, a candle was designed which utilized the principle of the M2 candle, except that the hot gaseous products of combustion of the fuel were mixed with air from the atmosphere to cool the gases so that the toxic agent could be volatilized at a lower temperature. This type of candle became known as the Comings Candle, named after the inventor.

The general design of the candle is shown in figs. 3, 4, 5, 6, 7, and 8. The agent is contained in an upper compartment, and the fuel, which burns in the absence of air, is held in a lower compartment, which is separate and can be detached from the upper compartment. In operation, radiant heat from the surface of the burning fuel is transmitted directly to the bottom of the agent compartment. This heat melts the agent and raises its temperature. Hot gases from the fuel block pass through a 13/32-in. orifice at a high velocity and entrain air in the throat of an injector. The liquid agent flows through a 0.204-in.-diam. hole into the throat of the injector and is broken into a fine spray by the high-velocity gas stream. Flow through this latter hole is caused by the pressure in the agent compartment, as well as by the hydrostatic liquid head. Droplets of liquid which are not evaporated in the gas stream are thrown out by the baffle and returned to the agent compartment to be recirculated. The gas stream and the vapor then pass through forty 1/8-in. holes on the top and side of the candle.

Figure 4 shows the complete candle as viewed from the air intake and gas-vapor exit side. Figure 5 is a picture of the fuel compartment. Figure 6 is the internal assembly of air inlet, entrainer tube, and the bottom of the agent compartment. Figure 7 is a view from below showing the 13/32-in. orifice. The roof of the upper part of the candle is clearly visible. Figure 8 is the upper part of the candle with the top removed, showing the baffle. Figure 9 shows a typical smoke cloud produced by the candle.

The fuel for the candle amounted to 1,400 g. and was made up as follows.

The starter was a small pressed disc of 20 g. of sulfurless meal powder with cellulose acetate as a binder. This sulfurless meal powder was made up in the proportions of 54.1 g. of potassium nitrate, 40 g. of silicon, and 5.9 g. of powdered charcoal. To 20 g. of this mixture was added 6 ml. of a 4.8% solution of cellulose acetate in acetone.

The main fuel block was composed of two layers: The upper layer was a mixture of 86 g. of ammonium nitrate which passed through a 60-mesh screen and 14 g. of charcoal which passed through a 200-mesh screen. This was mixed with 30 ml. of a 4.5% solution of celluloid in acetone. The main bottom layer was composed of 1,000 g. of ammonium nitrate, 163 g. of powdered charcoal, and 100 g. of ammonium chloride mixed with 300 ml. of the 4.5% solution of celluloid in acetone. The separate mixtures were added in layers and pressed under a pressure of a few tons load. After all the mixture was in the fuel block container, it was pressed under a total load of 25 tons. The completed block was dried in an oven for several hours or at room temperature for several days.

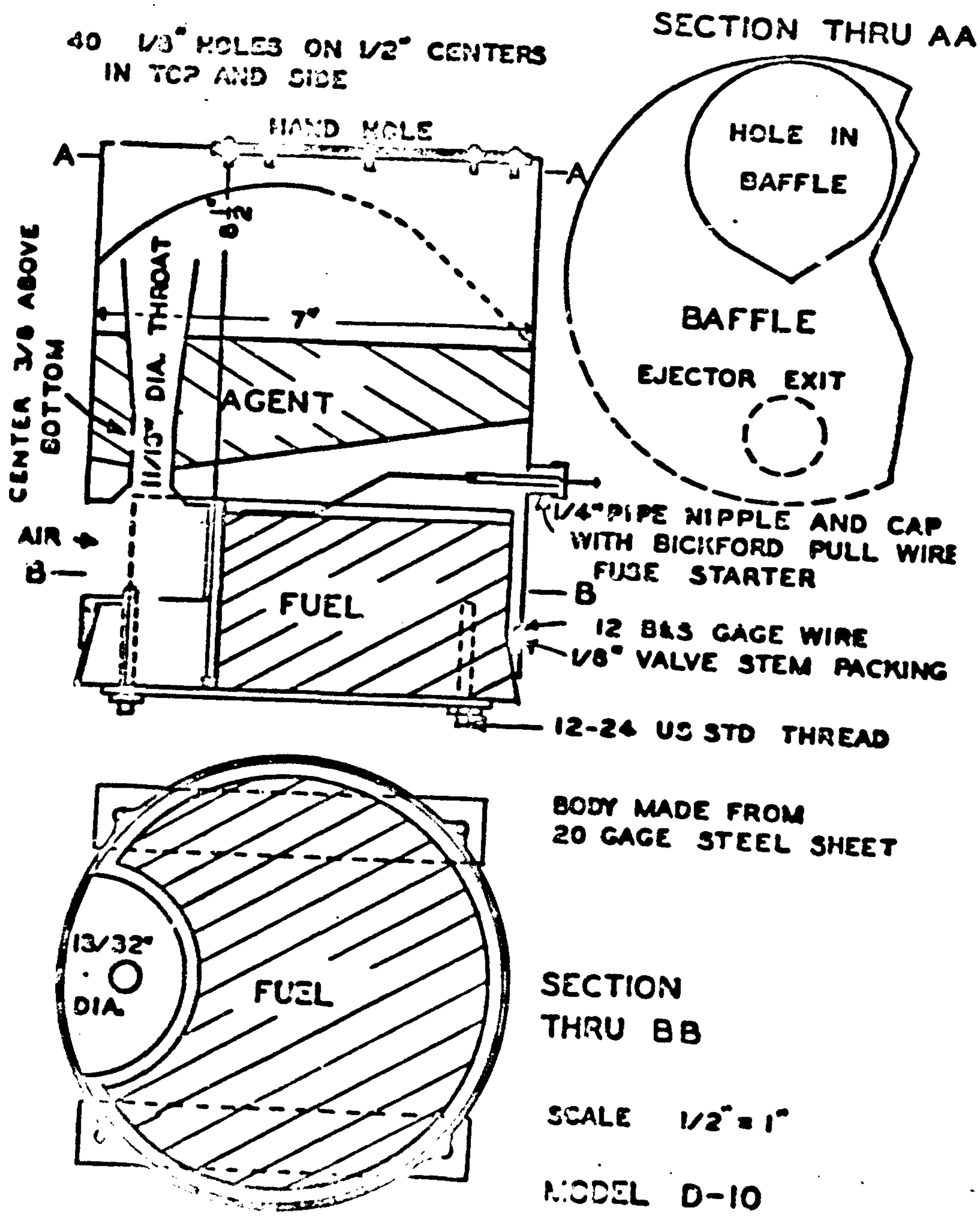

Figure 3.--GENERAL DESIGN OF COMINGS CANDLE

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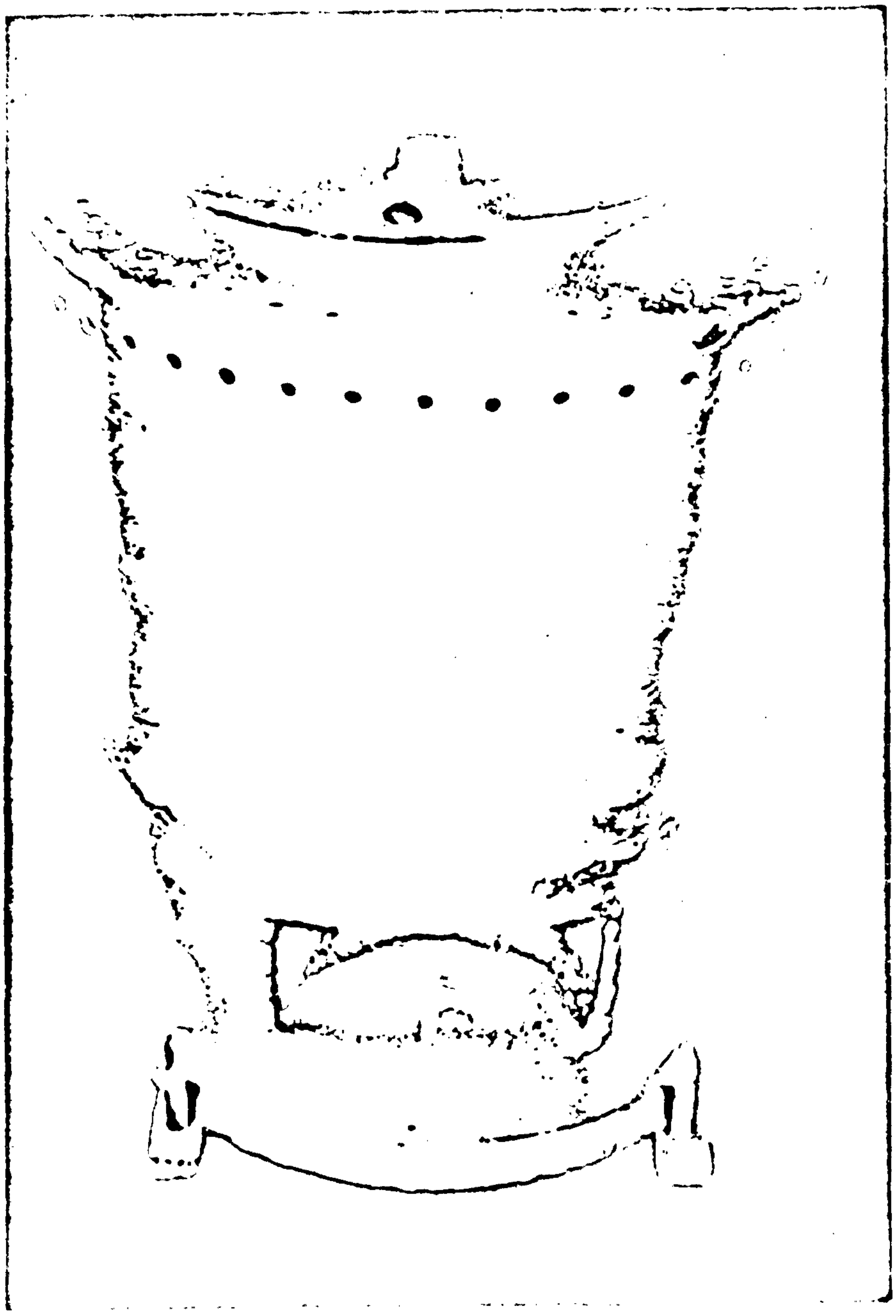

FIGURE [illegible]--MODEL D-[illegible]

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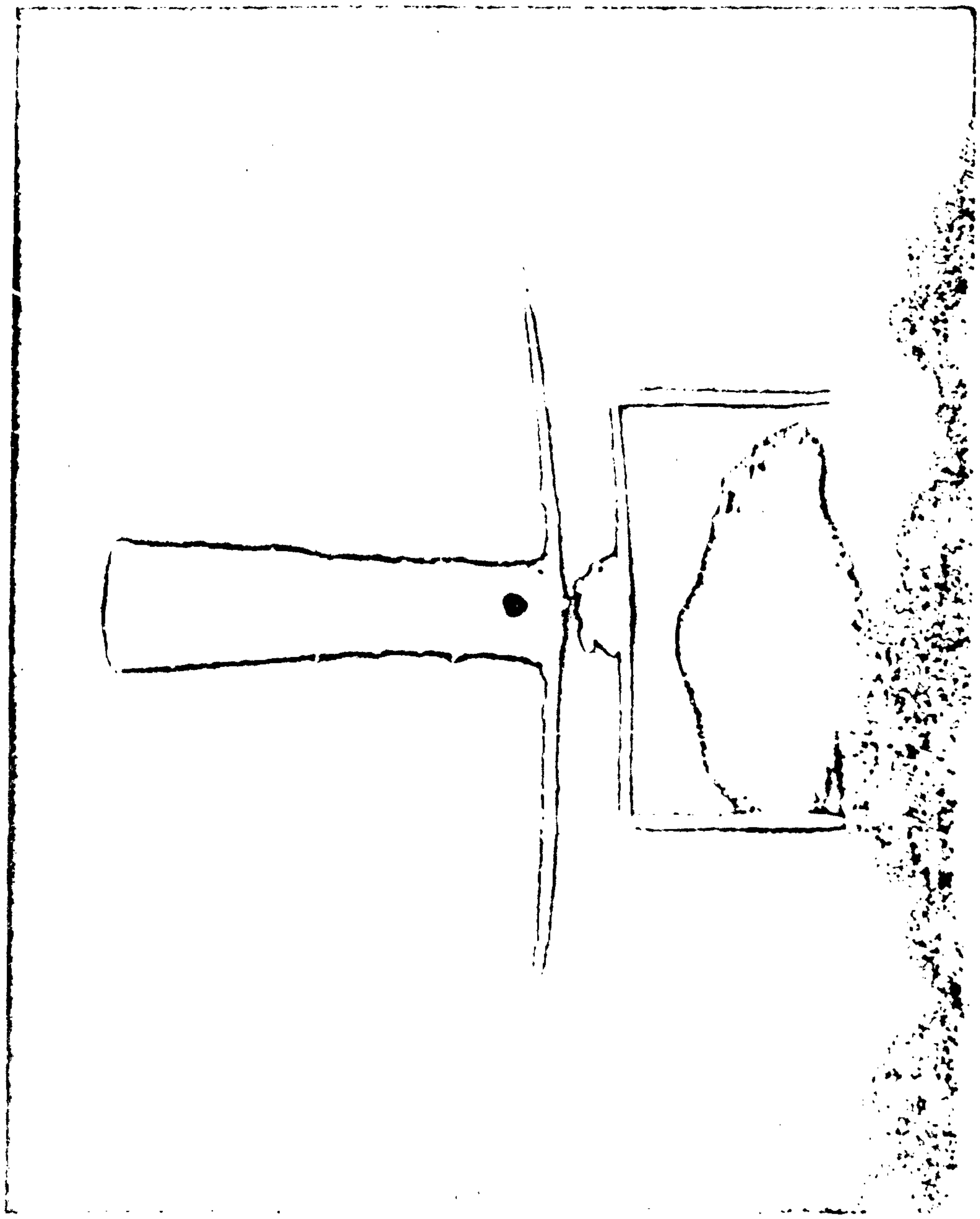
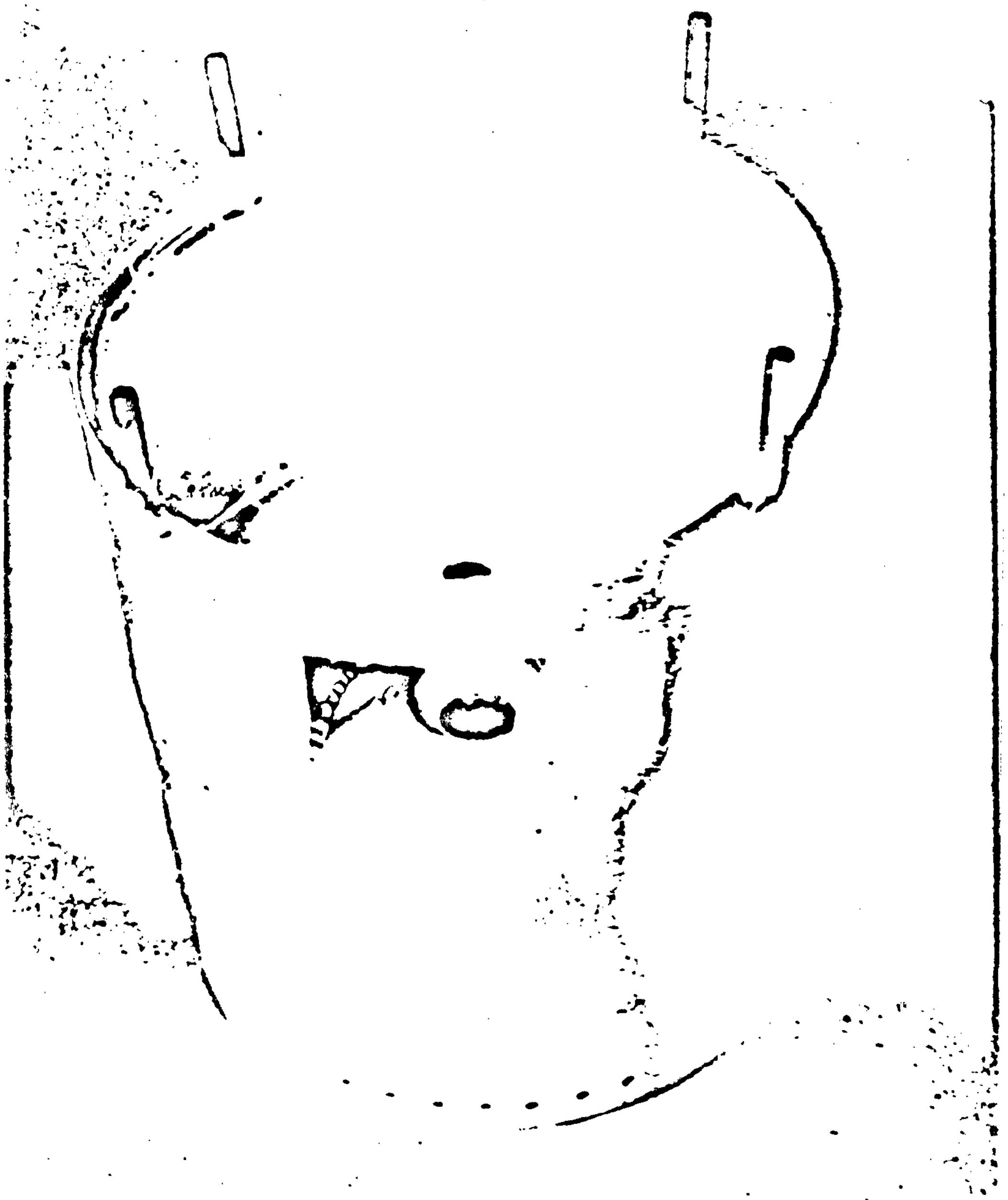


Figure 5.--FUEL COMPARTMENT D-10 MODEL



[illegible] --INTERNAL ASSEMBLY [illegible]

FIGURE [illegible]-D-10 [illegible] AIR INLET AND BOTTOM OF [illegible] COMPARTMENT

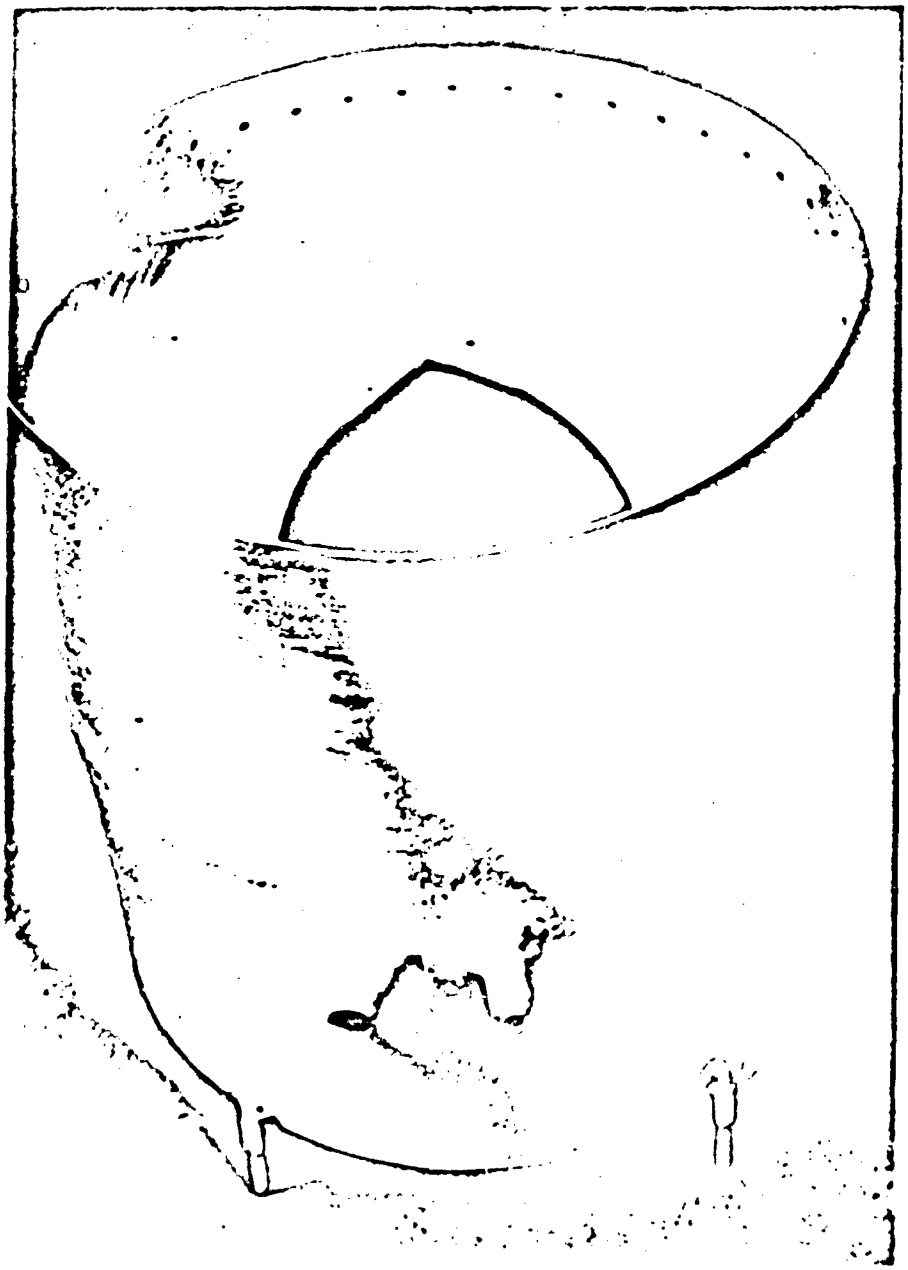


Figure [illegible]—VIEW OF D-10 [illegible] WITH TOP [illegible] SHOWING [illegible]

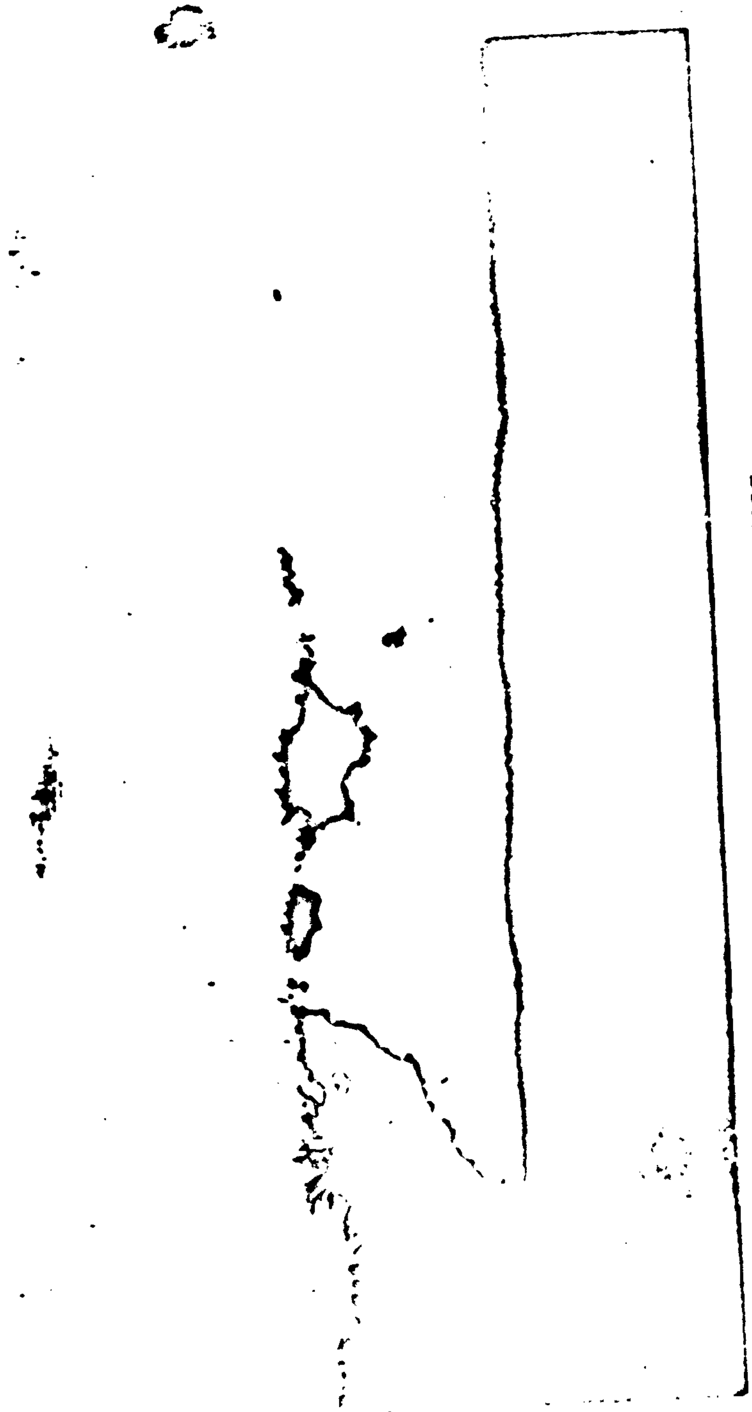


Figure 9.--SMOKE FROM D-10 CANDLE

Some of the special features of the candle should be noted. The use of an injector has several advantages. It provides one of the most effective ways of bringing about good contact between the hot gases and the liquid agent in a small space. This good contact results in the hot gases leaving the candle nearly saturated with vapor and permits the use of a lower liquid agent temperature in the candle, thus reducing the thermal decomposition. It also permits the use of a higher temperature in the fuel block since the hot gases are diluted with air before coming in contact with agent. The injector likewise gives a relatively high pressure in the agent compartment (15 to 30 in. of water), and this produces the necessary high velocity through the small 1/8-in. exit holes. The high velocity leads to a small particle size which is conducive to greater canister penetration.

A comparison of this candle with the M2 candle showed that in the case of DM, the Comings candle is only slightly more efficient than the M2 candle. This was due to the fact that DM shows good thermal stability at high temperatures for short periods of time. With the Comings candle 68% of the DM was dispersed as undecomposed smoke. With the M2 candle 56% of the DM was dispersed as undecomposed smoke.

In an experiment in which DC was dispersed by a Comings candle, 91% of the agent was undecomposed in the smoke (50).

Figure 10 shows a sectional diagram of the M2 DM candle, while figure 11 shows the candle in operation.

Grenade, Hand, Irritant CN-DM, M6. In 1932, The Lake Erie Chemical Company, Cleveland, Ohio, placed on the market a candle known as the "Lake Erie Lightning Universal K.O. and Tear Gas Candle." This candle contained the following mixture:

CN	16.0%
DM	16.0%
E.C. powder	65.4%
MgO	2.6%

During November, 1932, verbal instructions were received from the Office, Chief, Chemical Warfare Service, to prepare candles similar to the Lake Erie K.O. and Tear Gas Candle for test. These candles had been used by civil authorities a number of times for controlling mobs and riots and were found to be quite effective.

The candles made at Edgewood Arsenal, while similar to the Lake Erie candles, contained a higher percentage of both CN and DM than did the Lake Erie

50. "Toxic Smoke Candle and Screening Smoke Units," National Defense Research Committee (hereinafter NDRC) of the Office of Scientific Research and Development (hereinafter OSRD) Division 9, Progress Report, pp. 7, 9, 14, 25 Sep 1942. (In CRLTL as NDRC Misc. Pub. 158.); "I. Toxic Smoke Candle. II. Screening Smoke Units," NDRC Serial No. 440, p. 54, 1 Dec 1942. (OSRD 1076.)

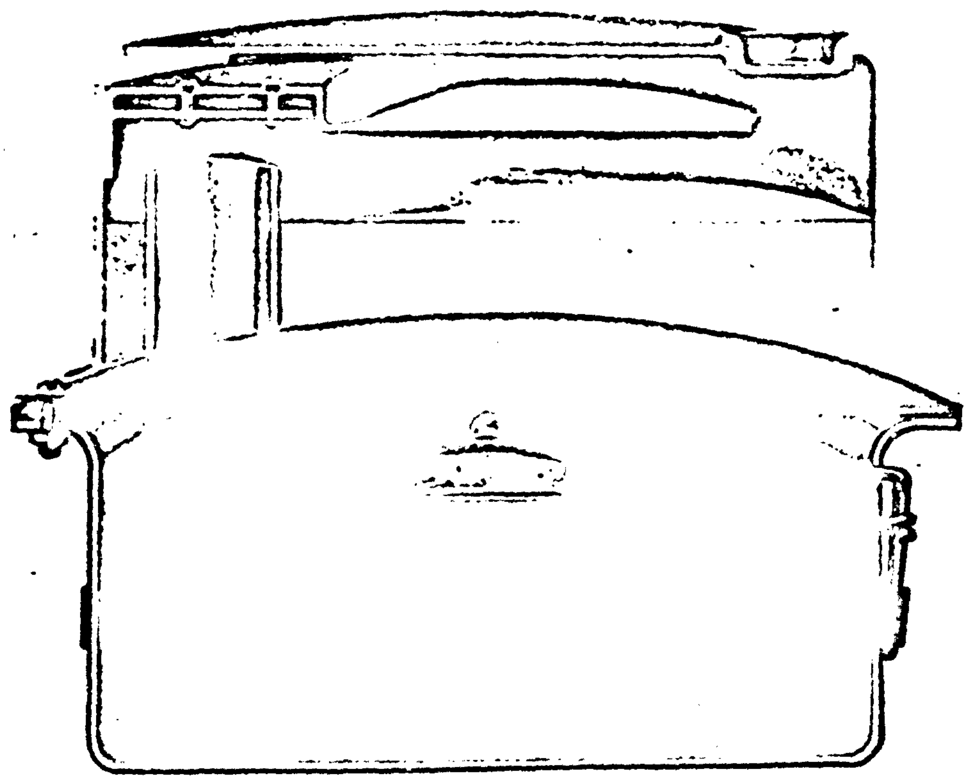


Figure 10.--DM CANDLE, M2
(Sectional diagram)

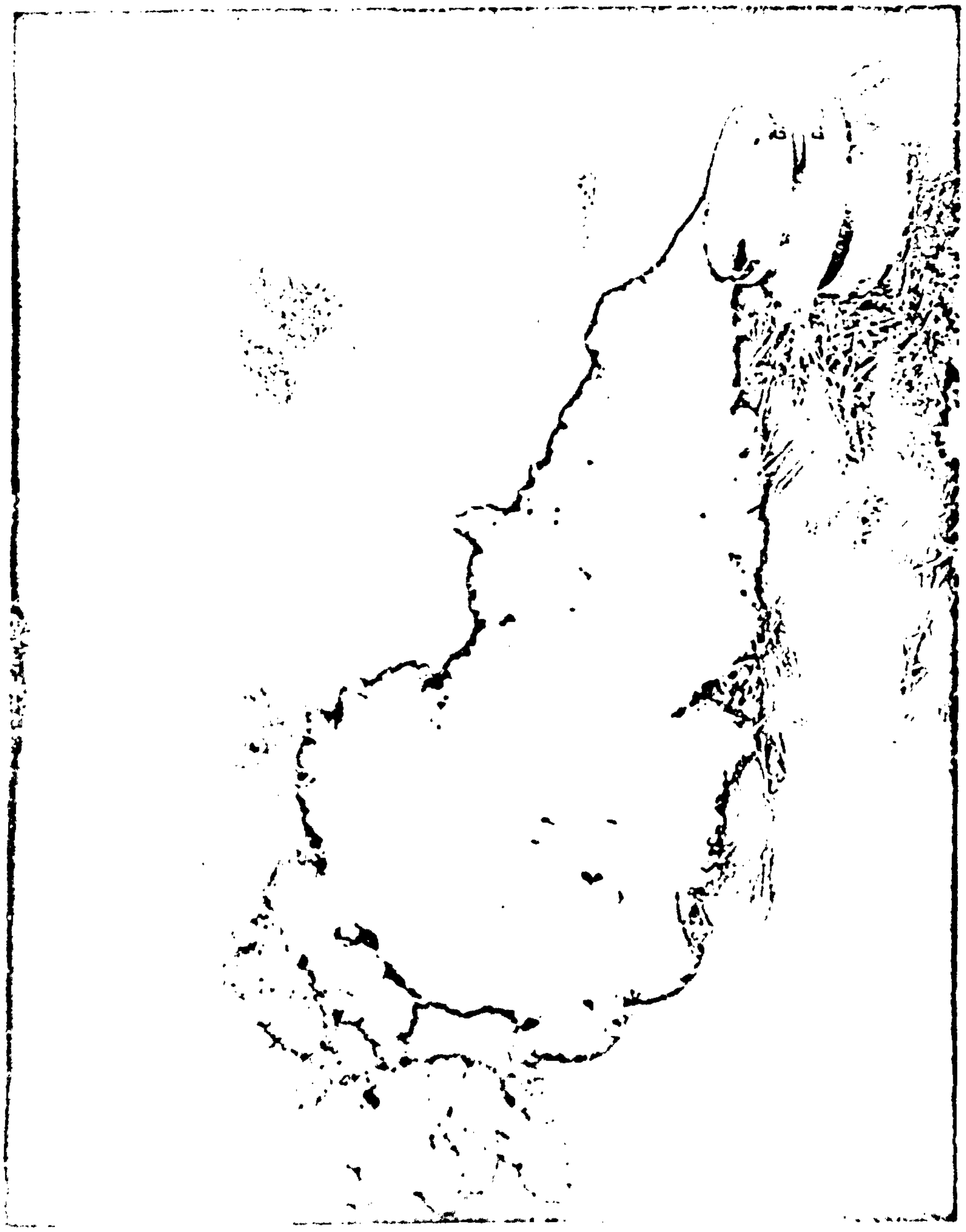


Figure 11.--DM CANDLE, M2 IN OPERATION

candles. The composition of the candles made and tested at Edgewood Arsenal was:

CN	21.0%
DM	21.0%
E.C. powder	55.4%
MgO	2.6%

These candles were made by loading into the fast-burning CN candle container approximately 290 g. of the mixture under a pressure of 4,700 lb./sq.in. Three slots, 3/8 in. by 3/8 in. at the top and 3/16 in. by 3/16 in. at the bottom, were left extending down the sides of the mix. These slots were placed equidistant around the sides of the mix. Three rows of six holes each, 5/32 in. in diameter, opening into the slots in the mix (one row opening into each slot) were in the sides of the container. The top also contained six 5/32-in. holes.

The starter used consisted of 5 g. of meal powder and a binder consisting of 4% celluloid and 96% acetone. The starter paste was made very thin and was poured on top of the mix and allowed to flow down into the slots on the side.

The candles have a burning time of 35 to 40 sec. A bright yellow cloud is produced (51). These candles were made standard items of CWS.

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51. "Irritant Hand Grenade (CN-DM) M6 (Fast CN-DM Irritant Candle M1)," EATR 151, pp. 3-4, 28 Jun 1933.

CHAPTER V

Standard Item

Grenade, Hand, Irritant, CN-DM, M6

Description. The irritant hand grenade CN-DM, M6, is designed in one size only, the 1.06-lb. The container is cylindrical in shape, 2.48 in. in diameter and 5.7 in. high. It is made of tin plate 0.014 in. thick, lock-seamed and soldered. The container is provided with three rows of six holes each. The holes are 5/32 in. in diameter. The rows of holes are perpendicular to the bottom of and spaced 120° apart on the circumference of the container. The holes are spaced approximately 0.66 in. apart in the rows. The top of the container is made of 0.021-in. tin plate and is crimped in place. The top contains, in addition to an adapter for the firing mechanism, six 5/32-in. holes radially located, and spaced 60° apart. The holes in both the container and top are covered with small squares of adhesive tape (see fig. 12) (52).

Data for Irritant Hand Grenade CN-DM, M6.

Nature	Irritant gas
Filling	Chloroacetophenone, diphenylamine-chloroarsine, and smokeless powder
Fuze	Igniting M201A1. Delay time 1.2-2.0 sec.
Weight	1.06 lb.
Burning time	20-60 sec.
Markings	"CN-DM" stenciled in 1-in. red letters above 1/2-in. red band, and "Gas" stenciled in 1-in. red letters below the band. Lot No. stenciled in 1/4-in. red letters around the bottom of the candle
Color	Blue-gray
Packing	Unit container, metal can; Shipping container, wooden box; 25 grenades to box. Shipping weight, approx. 50 lb. Cubage, approx. 1.8 cu.ft. A data and instruction card is packed in packing case.

52. Book of Standards, Chemical Warfare Service, p. 26, 15 Nov. 1951.

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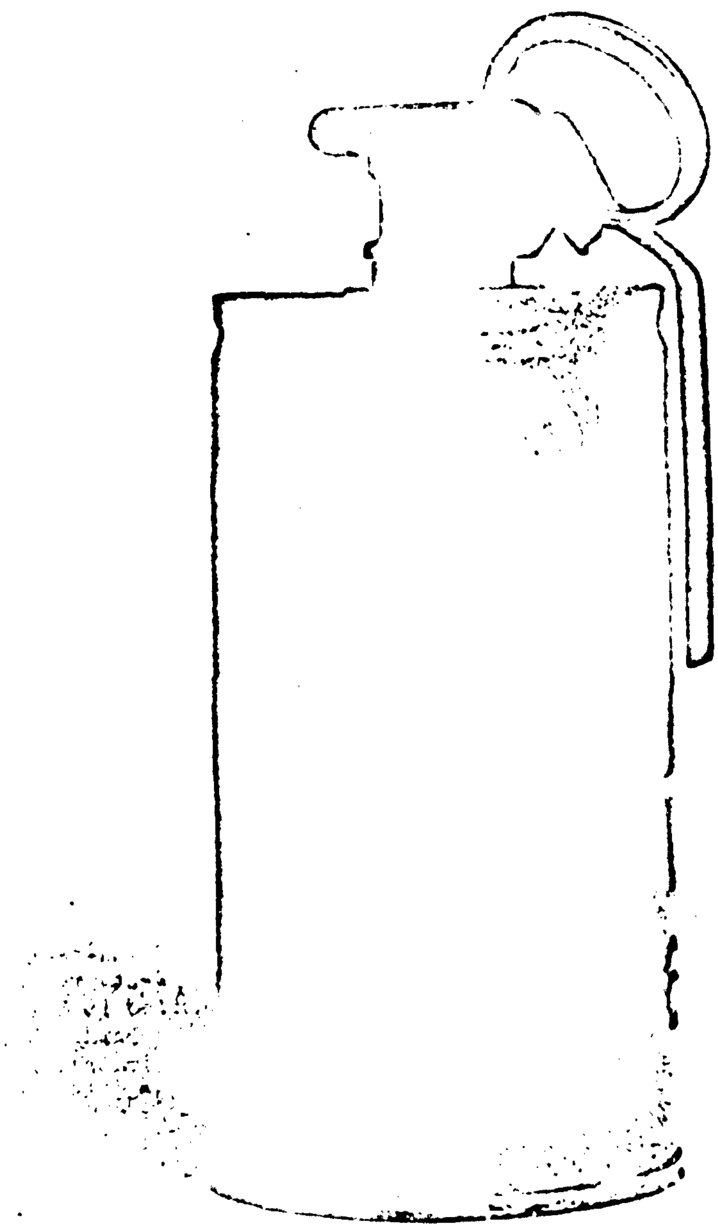

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Figure 12.--GRENADE, HAND, IRRITANT, CN-DM, M6

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Storage .... The candles should be stored in a cool, dry place. They should be given reasonable protection from excess moisture.

BIBLIOGRAPHY

	Footnote number
American University Experimental Station, Research Division, Chemical Warfare Service, (Washington, D. C.)	
——, C.P. (Chemical Production Section) 20, "Report on the Manufacture of Diphenylchloroarsine," 16 Aug 1918...............	22
——, D.S. (Dispersoid Section) 9, "Density and Rate of Settling of DA," 18 May 1918.....................................	10
——, D.S. 46, "Comparison of the Smokes Produced by Three Samples of DM," 28 Jun 1918................................	12
——, D.S. 51, "Effect of Temperature of the Efficiency of Production of Smokes by Explosive Dispersion," 10 Jul 1918.	12
——, D.S. 80, "The Dispersion of DA by the Explosive Method Using TNT and Tetryl," 8 Aug 1918...........................	11
——, D.S. 89, "A Comparison of the Quantity of Smoke Obtained From Similar Bombs Enclosed in Fragile and Strong Containers," 20 Aug 1918.................................	11
——, D.S. 90, "The Dispersion of CN by the Explosive Method," 21 Aug 1918..	10, 11
——, D.S. 95, "Effect of Aluminum Upon the Dispersive Power of an Explosive," 11 Sep 1918.................................	12
——, D.S. 114, "The Mixture Type of Dispersoid Shell," (undated)...	10
——, D.S. 115, "Penetration of G-76 Smokes Made by Explosive Dispersion in a 10 cu.m. Box," 21 Oct 1918................	11
——, D.S. 150, "The Use of Mixtures of DM and TNT in 75-Mm. Shell for the Production of Toxic Smokes," 17 Dec 1918.....	10
——, D.S. 155, "Development of a Shell for Efficient Dispersion of DA and Similar Toxic Substances," 25 Jan 1917..............	13
——, D.S. 159, "The Production of DM Smoke From 75-Mm. Shell, 23 Dec 1918...	12
——, G.M.R. (Gas Mask Research Section) 684, "Protection Afforded by Various Canisters Against DA Shells," 7 Oct 1918........	13
——, O.R. (Offense Chemical Research Section) 23, "Preparation of Diphenylchloroarsine and Phenyl Dichloroarsine From Triphenylarsine and Arsenic Trichloride (Sealed Tube Method)," 2 July 1918....................................	22
Chemical Corps Technical Committee Minutes, CCTC Item 2288, "Revised Military Characteristics for War Gases," 8 Mar 1951........	16
Chemical Defence Establishment (Sutton Oaks, England), Sutton Oaks Report 4??, "Diphenylcyanoarsine - Part V - The Physical Properties of HA, DA, TA, and DC," 4 Dec 1940.....	27, 32

	Footnote number
ical Defence Experimental Station (Porton, England), Porton Report,	
-, P.R. 417, "Report on Improvement of the Existing D.M. Generator," Part 1, Nov 1926	37
-, P.R. 2272, "Physical Constants of Arsenicals Related to D.C., 10 Sep 1941	32
ical Defence Research and Development, Ministry of Supply (Shell Mex House, Strand, London), Monograph No. 9.311, "Some Aspects of the Physical Chemistry of War Gases," Sep 1950. (In CRLTL as ETP 550 E-7736.)	27, 32, 37, 38
ical Warfare Service, Book of Standards, 15 Nov 1951	52
ical Warfare Service, Office of the Chief, "The Use of Arsenical Compounds During the World War," 8 May 1933. (In CRLTL as ETP 011-7.)	2, 5, 7
ical Warfare Service Project Program for 1929-1930 (Edgewood, Md.), Project Program F12a, "Manufacture of Chemicals for Experimental Purposes,"	24
wood Arsenal Chemical Division, Report,	
-, EACD 46, "Vapor Pressure of DM," 1 Jun 1921	37
-, EACD 127, "A Digest of Reports Concerning the Toxic Effect of Diphenylchloroarsine," 5 Apr. 1922	1
-, EACD 225, "The Development of the Manufacture of Diphenylchloroarsine (D.A.) on a Semi-Works Basis," 8 Nov 1922	21
-, EACD 241, "9-Pound D.M. Candle," 1 Feb 1924	48
-, EACD 259, "Development of a Method for the Manufacture of Diphenylchloroarsine," 22 Mar 1923	17, 19
-, EACD 298, "Design and Construction of a Small Scale Plant for the Manufacture of Diphenylchloroarsine," 24 Nov 1923	20
-, EACD 434, "The Development of the Sodium Process for the Manufacture of Diphenylchloroarsine," 19 Oct 1927	23, 25
wood Arsenal Technical Report,	
-, EATR 50, "Chemical Warfare Agents," 30 Jun 1931	26
-, EATR 78, "Constants and Physiological Action of Chemical Warfare Agents," 19 Jul 1932	27, 28, 30, 37, 39, 41
-, EATR 151, "Irritant Hand Grenade (CN-DM) M8 (Fast CN-DM Irritant Candle M1)," 28 Jun 1933	51

Footnote number

Edgewood Arsenal Technical Report (Contd.)
——, EATR [illegible], "Irritant Smokes, Preliminary Investigation," 18 Nov 1938 ... 4, 6, 8, 10, 11, 12, 13, 14, 36, 42
——, EATR 308, "Irritant Smoke, DM, DA, and Cyan-DA in 75-mm. Shell Status Report on Engineering Tests Under Project A2," 29 Nov 1939 ... 43

Interallied Control Commission, Sub-Commission on Armament, Chemical Section for Control of War Factories, Office of Engineering Powders. (undated). (In CRLTL as ETF 550, G-4.) ... 18

LaCoste W., and Michaelis, A., "Uber aromatische Arsenverbindungen," Justus Liebigs Annalen der Chemie, 201, 1880 ... 17
——, "Uber Mono- and Diphenylarsenverbindungen," Berichte der deutschen chemischen Gesellschaft 11, 1878 ... 17

Lake Erie Chemical Company (Cleveland, Ohio), Report No. 6120, Contract No. W-266-C.S-165, "Manufacturing Process for Diphenylcyanarsine Including Diphenylchloroarsine and Triphenylarsine," 9 Dec 1941. (In CRLTL as ETF 1C2C3-6.) ... 31, 33, 35

Michaelis, A., "Uber aromatische Arsenverbindungen," Justus Liebigs Annalen der Chemie, 321, 1902 ... 17

National Defense Research Committee of the Office of Scientific Research and Development, Div. B, Progress Report, "Toxic Smoke Candle and Screening Smoke Units," 25 Sep 1942. (NDRC Misc. Pub. 158) ... 50

National Defense Research Committee of the Office of Scientific Research and Development, Div. B, (University of Illinois), Report OSRD No. 1076, Serial No. 440, "I. Toxic Smoke Candle. II. Screening Smoke Units," 1 Dec 1942 ... 50

Prentiss, Augustin M., Chemicals in Warfare (New York: Mc Graw-Hill Book Company, Inc., 1937) ... 3, 9, 15

Sartori, Mario. The War Gases (New York: D. Van Nostrand Company, Inc., 1939) ... 29, 34, 36, 40

Technical Division Memorandum Report,
——, TDMR [illegible], "New Methods of Dispersing Chemical Agents. Low Temperature Fuels for Generating Toxic Smokes," 13 Feb 1940 ... [illegible]

Footnote number

nical Division Memorandum Report (Contd.)

--, TDMR 288, "Gas (2) for Navy HE-Gas Projectiles. Dispersion of Mixtures of Cyan DA and Cacodyl in 75-MM. Shell," 2 Jun 1941 44
--, TDMR 357, "Gas (2) for Navy HE-Gas Projectile. Dispersion of Mixtures of Cyan DA and Cacodyl in 105-MM. Projectiles in the Open," 10 Feb 1943 45
--, TDMR 363, "Gas (2) for Navy HE-Gas Projectiles Modified M60 105-MM. Projectiles Filled with a Mixture of Cyan DA and Cacodyl Impact Field Test of March 1, 1942," 6 Apr 1942.... 46
--, TDMR 365, "Gas (2) for Navy HE-Gas Projectile. Dispersion of Mixtures of DA and Cacodyl in 75-MM. Projectile," 29 Apr 1942 47
--, TDMR 456, "Data on Chemical Warfare," 25 Nov. 1942 28
--, TDMR 479, "Development of a New Fuel for the DM Candle," 5 Dec 1942 49

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